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Organometallic compounds of titanium, zirconium, and lanthanum

Reuben Gardner Jones
Iowa State College

ORGANOMETALLIC COMPOUNDS OF TITANIUM, ZIRCONIUM, AND LANTHANUM

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Reuben G. Jones

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Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

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INTRODUCTION

The future advances in organometallic chemistry will be largely dependent upon the preparation of new types and upon improvements in the methods of synthesizing many of the known RM compounds. It is remarkable that all attempts to prepare organometallic derivatives of almost half of the metals have been unsuccessful. In many cases, however, these attempts appear to have been very few in number. For instance, the chemical literature contains no reports on reactions for the preparation of organometallic derivatives of the rare earth metals. On the other hand, numerous efforts have been made to synthesize organovanadium and organoiron compounds, as well as the organometallic compounds of many of the other transition metals, but none has met with success. The fact that organometallic derivatives of several typical transition metals, notably platinum and chromium, do exist lends hope that organometallic compounds of all of the metals may eventually be prepared. This hope is further heightened by the recent reports on the preparation of organomolybdenum and organotungsten compounds.

The original aim of the work reported in this thesis was to prepare, if possible, some typical organometallic compounds of some of the transition elements. The metals

selected were titanium, zirconium, and lanthanum. An examination of the literature revealed that several studies on the attempted synthesis of organotitanium compounds had been reported but that few studies had been made on zirconium and lanthanum compounds. Before any experiments were undertaken, it seemed necessary to have available a collection of all of the known methods for preparing organometallic compounds. Such a collection of methods is included in the HISTORICAL section of this thesis. A number of these methods were then applied to titanium, zirconium, and lanthanum. Although the primary objective of this work was not realized, some interesting and important results were obtained on the reactions of the halides with Grignard reagents and organolithium compounds.

HISTORICAL

General Methods of Preparing Organometallic Compounds

In this review of the general methods of preparing organometallic compounds, no attempt has been made to include all references on the preparation of all organometallic compounds. For each method, only one or two examples have been cited. Probably some important references have unintentionally been omitted, but an attempt has been made to include the more recent literature citations from which information on previous related work can usually be obtained.

In 1927, Garzuly (1) listed seven general methods for the preparation of organometallic compounds. Actually, today there are at least twenty-eight different methods that have been used to prepare various organometallic compounds. Naturally all of these reactions cannot be applied to the preparation of organometallic compounds of each metal. Organometallic derivatives of some metals can be obtained by only one or two of the general methods. Also, some of the special methods to be considered here can be used with only one or two closely related metals.

(1) Garzuly, "Organometalle", Vol. XXIX of Herz' "Sammlung chemisch und chemisch-technischer Vorträge", Enke, Stuttgart (1927), p. 319.

The various reactions will be discussed under three main headings: preparations involving free metals; preparations from metal salts; and, preparations from other RM compounds of the same metal (interconversion methods). The following is a summary of the processes in the order in which they will be considered:

I. Methods Involving Free Metals

1. $2M + RX \longrightarrow RM + MX$
2. $2M + ROR \longrightarrow RM + MOR$
3. $M + RH \longrightarrow RM + H$
4. $MM' + RX \longrightarrow RM + M'X$
5. $M + RM' \longrightarrow RM + M'$
6. $M + RM' \xrightarrow{\text{electrolysis}} RM + M'$
7. $M + \text{ketone} \xrightarrow{\text{electrolysis}} RM$
8. $M + R. \longrightarrow RM$
9. $M + \text{double bond} \longrightarrow RM$
10. $2M + R\text{-}R' \longrightarrow RM + R'M$

II. Methods Involving Metal Salts

1. $MX + RM' \longrightarrow RM + M'X$
2. $MX + 2RM' + RX \longrightarrow R_2M + 2M'X$
3. $MX + RX + Na \longrightarrow RM + NaX$
4. $MX + RX \longrightarrow RMX_2$
5. $MX + Al_4C_3 \longrightarrow CH_3M$
6. $MX + RH \longrightarrow RM + HX$
7. $MX + \text{olefinic double bond} \longrightarrow RM$
8. $MX + ArN_2Cl \longrightarrow ArM + N_2$

9. $RCOOM \xrightarrow{heat} RM + CO_2$

10. Special methods for organomercury compounds

III. Preparations from RM Compounds

1. $RM + R'M' \longrightarrow R'M + RM'$

2. $RM + R'H \longrightarrow R'M + RH$

3. $RM + R'X \longrightarrow R'M + RX$

4. $RMM' + R'X \longrightarrow RR'M + M'X$

5. $2RMX \longrightarrow R_2M + MX_2$

6. RM + olefinic double bond $\longrightarrow$ R'M

7. $RM + RX \longrightarrow R_2MX$

8. $RMX \xrightarrow{reduction} RM$

I. Methods Involving Free Metals

1. Reactions of Metals with Organic Halides.--Although it cannot be applied to all metals, the reaction $2M + RX \longrightarrow RM + MX$, is perhaps the most fundamental reaction in organometallic chemistry. Upon it depend the syntheses, either directly or indirectly, of almost all organometallic compounds.

The reaction between lithium and organic halides is a general method for preparing RLi compounds. v. Grosse (3) prepared triphenylmethyllithium from 0.5% lithium amalgam and triphenylmethyl chloride in ether solution. Ziegler and Colonius (3) obtained good yields of phenyllithium from

(2) v. Grosse, Ber., 59, 2646 (1926).
(3) Ziegler and Colonius, Ann., 479, 135 (1930).

lithium and iodo- or bromobenzene and n-butyllithium from lithium and n-butyl halides in various solvents. The studies of Gilman and co-workers (4) established the reaction as one of choice for preparing ether solutions of a large number of RLi compounds.

Metallic sodium reacts with organic chlorides under carefully controlled conditions to give satisfactory yields of RNa compounds. n-Amylsodium was obtained from n-amyl chloride and sodium sand in petroleum ether (5). Chlorobenzene and p-chlorotoluene in petroleum ether, benzene, or toluene gave, with sodium sand, high yields of the corresponding RNa compounds (6). Recently, 20 to 25% yields of n-butylsodium and n-propylsodium were obtained by this method (7).

Like triphenylmethyllithium the corresponding triphenylmethylrubidium and triphenylmethylcesium were obtained from triphenylmethyl chloride and amalgams of the metals (3).

When ether solutions of certain alkyl and aryl halides were heated with beryllium powder at 80 to 90° for fifteen hours or longer, reactions took place with the formation of RBeX compounds (8). A catalyst, such as $HgCl_2$, or the less

(4) (a) Gilman, Zoellner and Selby, J. Am. Chem. Soc., 55, 1252 (1933).
(b) Gilman, Zoellner, Selby and Boatner, Rec. trav. chim., 54, 584 (1935).
(5) (a) Morton and Heckenbleikner, J. Am. Chem. Soc., 58, 1697 (1936).
(b) Morton and Richardson, ibid., 62, 123 (1940).
(c) Gilman and Pacevitz, ibid., 62, 1301 (1940).
(6) Gilman, Pacevitz and Baine, ibid., 62, 1514 (1940).
(7) Morton, Richardson and Hallowell, ibid., 63, 327 (1941).
(8) Gilman and Schulze, ibid., 49, 2904 (1927).

effective $BeCl_2$, was necessary. The compounds CH_3BeI, C_2H_5BeI, C_2H_5BeBr, n-C_4H_9BeI, and C_6H_5BeI were prepared by this method.

Little need be said of the well known reaction between magnesium and organic halides in ether solution to give Grignard reagents, named after their discoverer (9). Some interesting variations of this reaction have been reported. An 85% yield of phenylmagnesium chloride has been obtained by heating chlorobenzene with magnesium in a sealed tube at 150 to 160° (10). It has been claimed that high yields of RMgX compounds result from the reaction of magnesium with alkyl or aryl halides in the absence of any solvent if only a little ethyl orthosilicate is present (11). Dialkyl sulfates react with magnesium to give $RMgOSO_2R$ compounds (12), but the presence of a trace of magnesium halide is necessary for the reaction to occur (13).

Employing the same technique as for the preparation of Grignard reagents, one may cause calcium to react with organic iodides to yield RCaI compounds. This reaction, first studied by Beckmann (14), is apparently limited to aryl iodides and

(9) Grignard, Compt. rend., 130, 1322 (1900).
(10) Gilman and Brown, J. Am. Chem. Soc., 52, 3330 (1930).
(11) Andrianov and Gribanova, J. Gen. Chem. (U.S.S.R.), 8, 557 (1938) /C.A., 32, 7892 (1938)/.
(12) Suter and Gerhart, J. Am. Chem. Soc., 55, 3496 (1933).
(13) (a) Cope, ibid., 56, 1578 (1934).
(b) Suter and Gerhart, ibid., 57, 107 (1935).
(14) Beckmann, Ber., 38, 904 (1905).

primary alkyl iodides (15), although a slow reaction between calcium and secondary alkyl iodides was reported to take place (16). Phenylcalcium iodide has been prepared from calcium and iodobenzene in ether solution (17).

The reactions of strontium and barium amalgams with ethyl iodide have given evidence for the formation of small quantities of C_2H_5SrI and C_2H_5BaI (18). Other workers (19) have been unable to confirm the reaction of barium amalgam with ethyl iodide. These same investigators did, however, obtain small yields of ethylbarium iodide and phenylbarium iodide from electrolytic barium and highly purified iodides.

Early studies by Frankland (20) on the reaction between ethyl iodide and zinc led to the discovery of the first organometallic compound, ethylzinc iodide, which upon heating produces diethylzinc and zinc iodide. The reaction takes place more easily between ethyl iodide and a zinc-copper couple (21), and by this method Dennis and Hance (22) have prepared high yields of pure diethylzinc.

(15) Gilman and Schulze, J. Am. Chem. Soc., 48, 2463 (1926).
(16) Glacet, Bull. soc. chim., 5, 895 (1938).
(17) Gilman, Kirby, Lichtenwalter and Young, Rec. trav. chim., 55, 79 (1936).
(18) Krause and v. Grosse, "Chemie der Metall-Organischen Verbindungen", Gebruder Borntraeger, Berlin (1936), p. 123.
(19) Gilman and Schulze, Bull. soc. chim., 41, 1333 (1927).
(20) Frankland, Ann., 71, 171 (1849); 85, 329 (1853); 111, 44 (1859).
(21) Lachman, Am. Chem. J., 24, 31 (1900).
(22) Dennis and Hance, J. Am. Chem. Soc., 47, 370 (1925).

Unlike zinc, cadmium does not react easily with alkyl iodides. Wanklyn (23) probably prepared small quantities of diethylcadmium by the action of ether solutions of ethyl iodide on cadmium metal. Löhr (24) obtained only very small amounts of impure dimethylcadmium by heating cadmium with methyl iodide.

Maynard (25) has obtained high yields of methylmercuric iodide and benzylmercuric iodide from metallic mercury and the corresponding alkyl iodides. The reactions took place only in sunlight or other strong illumination. The only other organic halides which have reacted with mercury are ethyl iodide (26) and methylene iodide (27); also, α-bromophenylacetonitrile has been reported to react with mercury and give the compound, $C_6H_5CH(CN)HgBr$ (28).

Methylene iodide with aluminum, on long standing, gave a white reaction product (29). The reaction has been represented by the equation (30)

$$3CH_2I_2 + 4Al \longrightarrow 3CH_2AlI + AlI_3$$

Aluminum, activated with iodine, reacted readily with methylene bromide to give an organoaluminum compound of

(23) Wanklyn, J. Chem. Soc., 9, 193 (1856).
(24) Löhr, Ann., 261, 48 (1891).
(25) Maynard, J. Am. Chem. Soc., 54, 2108 (1932).
(26) (a) Frankland, J. Chem. Soc., 3, 322 (1851); Ann., 111, 44 (1859).
(b) Stecker, ibid., 92, 75 (1854).
(27) Sakurai, J. Chem. Soc., 37, 658 (1880); 41, 360 (1882).
(28) Kretov and Abramov, J. Gen. Chem. (U.S.S.R.), 7, 1572 (1937) [C.A., 31, 8518 (1937)].
(29) Thomas, Compt. rend., 174, 464 (1922).
(30) Faillebin, ibid., 174, 112 (1922).

unknown composition. This compound, with water, evolved pure methane (31). The high-boiling, oily product obtained from the reaction of ethyl iodide and aluminum at elevated temperatures (32) was thought, by Cahours (33), to be $(C_2H_5)_3Al \cdot AlI_3$. More recently, this product has been separated by fractional distillation (34) into $(C_2H_5)_2AlI$ and $C_2H_5AlI_2$. Spencer and Wallace (35) observed reactions between aluminum and a variety of organic halides with the probable formation of organoaluminum compounds, but in all cases the reaction products were treated with water, and, consequently, no organoaluminum derivatives were isolated. Recent investigations (36) have shown that the reaction of aluminum with organic halides is a method of choice for making organoaluminum compounds. Aluminum-copper alloy (8% Cu) and methyl chloride (36a), with 0.1% $AlCl_3$ as catalyst, reacted to give an equimolar mixture of dimethylaluminum chloride and methylaluminum dichloride in an almost quantitative yield. Similar reactions took place between aluminum and methyl bromide, methyl iodide, ethyl halides, n-propyl iodide, iodobenzene, and p-iodotoluene (36b) When methanol vapor was passed over aluminum filings at 270°,

(31) Ref. 18, p. 227.
(32) Hallwachs and Shafarik, Ann., 109, 206 (1859).
(33) Cahours, ibid., 114, 242 (1860).
(34) Grignard and Jenkins, Compt. rend., 179, 89 (1924).
(35) Spencer and Wallace, J. Chem. Soc., 93, 1827 (1908).
(36) (a) Hnizda and Kraus, J. Am. Chem. Soc., 60, 2276 (1938).
(b) v. Grosse and Mavity, J. Org. Chem., 5, 106 (1940).

the liquid condensate contained aluminum, apparently $(CH_3)_3Al$ (37).

Indium and thallium showed evidence of reacting when heated with iodobenzene and α-bromonaphthalene, but no products were isolated (35). Schumb and Crane (38) observed a very slow reaction between methylene iodide and indium, but they isolated no organoindium compounds. Under certain conditions metallic thallium reacted with organic iodides, apparently, according to the equation

$$3RI + 2Tl \longrightarrow R_3TlI + RTlI_2$$

This reaction will be considered in a later section.

Frankland (39) discovered that metallic tin reacted with ethyl iodide to give diethyltin diiodide. In the same way, methyl iodide and tin yielded dimethyltin diiodide (40). Finely divided metallic lead and ether solutions of organic iodides appeared to react readily. The conditions for these reactions will be considered in detail later.

At 160 to 200° methyl iodide and arsenic reacted to produce $(CH_3)_4AsI$, which, upon distillation over solid potassium hydroxide, gave trimethylarsenic (41). Methyl iodide and ethyl iodide with antimony in sealed tubes heated to 140° reacted to give the R_3SbI_2 compounds (42). A reaction

(37) Tropsch and Schellenberg, Abhandl. Kenntniss Kohle, 7, 13 (1925) /Chem. Zentr., 97, (1) 3298 (1926)/.
(38) Schumb and Crane, J. Am. Chem. Soc., 60, 306 (1938).
(39) Frankland, Ann., 85, 329 (1853).
(40) Cahours, ibid., 114, 367 (1860).
(41) Cahours, ibid., 122, 198 (1862).
(42) Buckton, J. Chem. Soc., 13, 115 (1861).

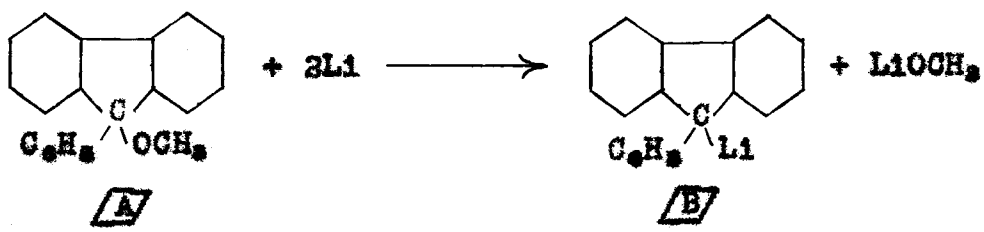
of selenium with methyl iodide at 180° led to the formation of the compound, $(CH_3)_2SeI \cdot I_2$ (43). Tellurium, in sealed tubes with methyl iodide (44) and with ethyl iodide (45) reacted, upon heating, to yield the corresponding R_2TeI_2 compounds.

3. Cleavage of Ethers.---Analogous with the reactions just described between metals and organic halides are the reactions of ethers with metals to give organometallic compounds and metal alkoxides.

$$ROR + 2M \longrightarrow RM + MOR$$

These reactions are apparently confined to the alkali metals.

Schlenk and Bergmann (46) studied the action of lithium on several methyl ethers. For example, compound /A/ reacted with lithium to give the organolithium compound /B/.



/A/ /B/

Apparently, also, a small quantity of $(C_6H_5)_2C(OCH_3)Li$ resulted when lithium stood in contact with $(C_6H_5)_2C(OCH_3)_2$ for three weeks (47). Sodium cleaved diphenyl ether, when

(43) Scott, Proc. Chem. Soc., 20, 156 (1904) /Chem. Zentr., 75, (2) 414 (1904)/.
(44) Demarcay, Bull. soc. chim., 40, 99 (1883); Drew, J. Chem. Soc., 564 (1929).
(45) Gilbert and Lowry, J. Chem. Soc., 3179 (1928).
(46) Schlenk and Bergmann, Ann., 463, 98 (1928).
(47) Schlenk and Bergmann, Ibid., 464, 35 (1928).

heated to 180°, to give phenylsodium and sodium phenoxide (48). With the ethyl naphthyl ethers and ethyl phenyl ether all four possible sodium compounds were formed by cleavage.

$$ROR' + Na \longrightarrow RNa + NaOR' + R'Na + NaOR$$

Ziegler and Thielmann (49) cleaved various ethers with potassium. For example, triphenylmethylpotassium resulted from the following reaction

$$(C_6H_5)_3COR + K \longrightarrow (C_6H_5)_3CK + KOR$$

Sodium-potassium alloy was found to cleave a variety of methyl ethers of the type $ROCH_3$ to give the corresponding RK compounds (50).

3. Direct Metalation.---The displacement of hydrogen from a hydrocarbon by a metal according to the reaction, $RH + M \longrightarrow RM + H$, occurs only if the metal is highly reactive and the hydrocarbon contains an active hydrogen atom. When acetylene was passed into a solution of sodium in liquid ammonia, hydrogen was evolved and a quantitative yield of ethynylsodium resulted (51). Sodium reacts with phenylacetylene also according to the equation

$$C_6H_5C{\equiv}CH + Na \longrightarrow C_6H_5C{\equiv}CNa + H$$

Gilman and Young (52) used this same sort of reaction to

(48) Schorigin, Ber., 56, 176 (1923).
(49) Ziegler and Thielmann, ibid., 56, 1740 (1923).
(50) Ziegler and Schnell, Ann., 437, 227 (1924).
(51) Hess and Munderloh, Ber., 51, 377 (1918).
(52) Gilman and Young, J. Org. Chem., 1, 315 (1936).

prepare the phenylethynyl derivatives of potassium, rubidium, and cesium. Lithium was found to be inert toward phenylacetylene (52). The reaction between calcium and acetylene in liquid ammonia gave good yields of diethynylcalcium (53).

$$Ca + 2C_2H_2 \longrightarrow HC{\equiv}C\text{-}Ca\text{-}C{\equiv}CH$$

Triphenylmethane reacted readily with the alkali metals in liquid ammonia solution with the evolution of hydrogen and the formation of the triphenylmethylmetallic compounds (54).

4. Reactions of Alloys with Organic Halides.--In some cases, where metals react only slowly or not at all with organic halides, it has been found advantageous to employ an alloy containing an alkali metal, usually sodium. The reaction may be represented by the equation

$$RX + M\text{-}Na \longrightarrow RM + NaX$$

Frankland and Duppa (55), long ago, used sodium amalgam to prepare R_2Hg compounds from organic halides. More recently, alkyl sulfates have been used (56).

$$R_2SO_4 + Hg\text{-}Na \longrightarrow R_2Hg + Na_2SO_4$$

A reaction of alkyl halides with an aluminum-magnesium alloy (30% magnesium) gave high yields of R_2AlX compounds (36b).

$$RX + Al\text{-}Mg \longrightarrow R_2AlX + MgX_2$$

(53) Vaughn and Danehy, Proc. Ind. Acad. Sci., 44, 144 (1935).
(54) Kraus and Rosen, J. Am. Chem. Soc., 47, 2739 (1925).
(55) Frankland and Duppa, Ann., 130, 104 (1864).
(56) Fuchs, J. prakt. Chem., 119, 209 (1928).

Sodium-tin alloy reacted with methyl and ethyl iodides to produce the R_2SnI and R_4Sn compounds (41). A sodium-tin alloy and bromobenzene gave Polis (57) tetraphenyltin.

The commercial production of tetraethyllead from ethyl chloride and sodium-lead alloy need not be discussed here. This same type of reaction was used by Cahours (58) to prepare tetramethyllead from methyl iodide, and by Polis (59) to make tetraphenyllead from bromobenzene. A rather unexpected reaction between sodium-lead alloy and acetone has been reported to yield triisopropyllead (60).

Sodium and potassium alloys of the fifth group metals, arsenic, antimony, and bismuth, have been employed for the preparation of organometallic compounds of these elements. Sodium arsenide heated with ethyl iodide (61a) and with methyl iodide (61b) gave the corresponding R_3As compounds. p-Bromoanisole and sodium antimonide at high temperatures formed tri-p-methoxyphenylantimony but in rather poor yields (62). Potassium-antimony alloys with alkyl iodides were used in the first studies on organoantimony compounds (63).

(57) Polis, Ber., 22, 2915 (1889).
(58) Cahours, Ann., 122, 48 (1862).
(59) Polis, Ber., 20, 716 (1887).
(60) Goldach, Helv. Chim. Acta., 14, 1436 (1931).
(61) (a) Landolt, Ann., 89, 301 (1854).
(b) Cahours and Riche, ibid., 92, 361 (1854).
(62) Loeloff, Ber., 30, 2834 (1897).
(63) (a) Loewig and Schweizer, Ann., 75, 315 (1850).
(b) Landolt, ibid., 78, 91 (1851).

Trialkylbismuth compounds were formed in the reactions of alkyliodides with potassium-bismuth alloys (63a, 64). Sodium-bismuth alloys have been used in the synthesis of triaryl-bismuth derivatives (65).

Aliphatic iodides heated with sodium hydroselenide yielded the corresponding RSeH compounds (66). A similar reaction was shown to take place between sodium ethyl sulfate and sodium hydroselenide (67). p-Nitrochlorobenzene reacted with sodium selenide in the following manner (68)

$$p\text{-}NO_2C_6H_4Cl + Na_2Se \longrightarrow (p\text{-}NO_2C_6H_4)_2Se + NaCl$$

In 1840 Wöhler (69) obtained diethyltellurium by distilling a sodium or potassium alloy of tellurium with potassium ethyl sulfate.

$$K\text{-}Te + C_2H_5OSO_2K \longrightarrow (C_2H_5)_2Te$$

Aluminum telluride has been used to prepare organotellurium compounds from alkyl halides. By this reaction, for example, tellurocyclohexane, $CH_2CH_2CH_2TeCH_2CH_2$, was made from pentamethylene bromide (70).

(64) (a) Breed, ibid., 82, 106 (1852).
(b) Dönhaupt, J. prakt. Chem., 61, 399 (1854).
(65) (a) Michaelis and Polis, Ber., 20, 54 (1887).
(b) Michaelis and Marquardt, Ann., 251, 323 (1889).
(c) Gillmeister, Ber., 30, 2843 (1897).
(66) Tschugaeff, Ber., 42, 49 (1909).
(67) Siemens, Ann., 61, 360 (1847); Shaw and Reid, J. Am. Chem. Soc., 48, 520 (1926).
(68) Baker and Moffitt, J. Chem. Soc., 1732 (1930).
(69) Wöhler, Ann., 35, 111 (1840).
(70) Morgan and Burgess, J. Chem. Soc., 321 (1928).

5. Metal-Metal Displacement Reactions.--The displacement of a metal from one of its organometallic compounds by another metal is a very general reaction. This method has been used to prepare organometallic compounds of most of the metals. Reactions of this type are usually reversible and should be written, $M + RM' \rightleftharpoons RM + M'$, although in many cases the point of equilibrium lies far to one side or the other. Usually, a more reactive organometallic compound is formed in the reaction of a metal with a less reactive organometallic compound. In most of the studies involving this reaction, R_2Hg compounds have been employed as starting materials, and three reasons for this choice are obvious. First, organomercury compounds are of a low order of reactivity, and this favors the formation of organometallic compounds of most other metals. Second, a large variety of R_2Hg compounds are relatively easily available. Third, the separation of the reaction products, in this case mercury and the new RM compound, is much easier because of the liquid nature of mercury.

Schorigin (71) allowed lithium to react with a benzene solution of diethylmercury and obtained ethyllithium as evidenced by the formation of propionic acid upon carbonation. Schlenk and Holtz (72) prepared methyllithium, ethyllithium, propyllithium, and phenyllithium by the action of lithium on

(71) Schorigin, Ber., 43, 1938 (1910).
(72) Schlenk and Holtz, Ber., 50, 262 (1917).

the corresponding R_2Hg compounds.

$$2Li + R_2Hg \rightleftharpoons 2RLi + Hg$$

The reversibility of this reaction was demonstrated by shaking a cyclohexane solution of n-butyllithium with metallic mercury. Di-n-butylmercury and lithium amalgam were formed (3). Likewise, dibenzylmercury was formed by shaking an ether solution of benzyllithium with mercury (73).

A preparation of benzyllithium has been reported (73) from a reaction of lithium with benzylmagnesium chloride.

$$2Li + C_6H_5CH_2MgCl \longrightarrow C_6H_5CH_2Li + Mg + LiCl$$

The reaction of lithium with an excess of diethylzinc led to the formation of a solution of ethyllithium in diethylzinc (74). In the same way, solutions of ethyllithium in diethylcadmium and triethylaluminum have been prepared. Phenyllithium has been reported from the reactions of lithium with triphenylbismuth and with tetraphenyllead (75).

The double compound ethylsodium-diethylzinc was early prepared by Wanklyn (76) from diethylzinc and metallic sodium.

$$2Na + 3(C_2H_5)_2Zn \longrightarrow 2C_2H_5Na\cdot(C_2H_5)_2Zn + Zn$$

By the action of sodium on a benzene solution of diphenylmercury, Acree (77) obtained phenylsodium and sodium amalgam.

(73) Ziegler and Dersch, ibid., 64, 448 (1931).
(74) Hein, Petzchner, Wagler and Segitz, Z. anorg. allgem. Chem., 141, 161 (1925).
(75) Talalaeva and Kocheshkov., J. Gen. Chem. (U.S.S.R.), 8, 1831 (1938) /C.A., 33, 5819 (1939)/
(76) Wanklyn, Ann., 107, 125 (1858).
(77) Acree, Am. Chem. J., 29, 588 (1903).

The RNa compounds were not isolated in a pure state until 1917 when Schlenk and Holtz (72) prepared a series of organosodium compounds from sodium metal and R_2Hg compounds. These same workers carried out reactions of sodium with R_4Pb compounds and obtained organosodium derivatives, but the products were impure and could not be separated from the finely divided lead produced by the reactions. Alkylcadmium and alkylaluminum compounds have been heated with sodium to produce the corresponding RNa derivatives (74).

Not only lithium and sodium, but also, as v. Grosse (2) has shown, potassium, rubidium, and cesium react with diethylzinc to give the double compounds of the formula, $C_2H_5M\cdot(C_2H_5)_2Zn$.

Dimethylberyllium was reportedly formed in a reaction of beryllium with dimethylmercury (78). Gilman and Schulze (79) found that diphenylberyllium and di-p-tolylberyllium were readily prepared in an analogous manner.

$$Be + R_2Hg \longrightarrow R_2Be + Hg$$

Diethylmercury and di-n-butylmercury, however, failed to react with beryllium.

Good yields of a number of symmetrical R_2Mg compounds have been obtained by heating magnesium with the corresponding

(78) Lawroff, Bull. soc. chim., 41, 548 (1884).
(79) Gilman and Schulze, J. Chem. Soc., 2663 (1927).

R_2Hg derivatives in sealed tubes (80). From a reaction between magnesium, mercury, and the double compound, $C_2H_5Na \cdot (C_2H_5)_2Zn$, Wanklyn (81) obtained diethylmagnesium and sodium amalgam. The same reaction applies to zinc. A mixture of zinc, mercury, and ethylsodium-diethylzinc reacted to give sodium amalgam and diethylzinc. With mercury alone, ethylsodium reacted to give diethylmercury and sodium amalgam. These reactions, like those mentioned between RLi compounds and mercury, are examples of organometallic compounds of high reactivity reacting with metals to yield compounds of a lower order of reactivity. Other related examples will be mentioned later. In each case, the energy involved in forming an amalgam seems to be sufficient to cause the reaction to take place. Recently, phenyllithium has been reported to react with magnesium, tin, lead, arsenic, and antimony, as well as with mercury, to give phenyl derivatives of these metals (75). The fate of the lithium in these reactions was not disclosed. Possibly free radicals (Section 8) were involved since the reactions were carried out in ether-xylene solutions at 100 to 110°.

A diethylzinc solution of diethylcalcium was obtained

(80) (a) Löhr, Ann., 261, 72 (1891).
(b) Fleck, Ibid., 276, 129 (1893).
(c) Gilman and Brown, Rec. trav. chim., 49, 724 (1930).
(d) Schlenk, Ber., 64, 736 (1931).
(81) Wanklyn, Ann., 140, 353 (1866).

by warming metallic calcium with an excess of diethylzinc (74). Schulze (82), however, found no definite evidence for the formation of organometallic compounds of calcium, strontium, or barrium when these metals were heated with R_2Hg compounds in sealed tubes.

The production of dialkylzinc derivatives takes place readily when metallic zinc is heated with dialkylmercury compounds (83). Good yields of diphenylzinc have been obtained by heating an excess of zinc with diphenylmercury, either without a solvent (84) or in boiling xylene solution (85).

The reaction of even a large excess of metallic cadmium with dialkylmercury (83) or diarylmercury (84) compounds led to an equilibrium mixture containing both R_2Cd and R_2Hg. Actually, diphenylcadmium reacted with an excess of metallic mercury and was converted completely to diphenylmercury and cadmium amalgam (84, 86).

The formation of R_2Hg compounds from metallic mercury and the more reactive organolithium, sodium, and cadmium analogues has already been discussed. Triphenylthallium in ether solution also reacted with mercury metal and

(82) Schulze, Doctoral Dissertation, Iowa State College, (1927), p. 22.
(83) Frankland and Duppa, Ann., 130, 117 (1864).
(84) Hilpert and Grüttner, Ber., 46, 1675 (1913).
(85) Kozeschkow, Nesmejanow and Potrosow, ibid., 67, 1138 (1934).
(86) Unpublished study by F. J. Webb.

yielded diphenylmercury and thallium amalgam (87). Triphenylbismuth and metallic mercury, when heated together, reacted until an equilibrium was reached wherein diphenylmercury and triphenylbismuth were both present (84).

Mercury reduced diphenylthallium bromide to thallous bromide with the production of a high yield of diphenylmercury (87).

$$(C_6H_5)_2TlBr + Hg \longrightarrow (C_6H_5)_2Hg + TlBr$$

Analogous reactions between mercury and phenyllead chlorides in alcohol-acetone solutions yielded diphenylmercury. These reactions were represented by the equations (88)

$$(C_6H_5)_2PbCl_2 + Hg \longrightarrow (C_6H_5)_2Hg + PbCl_2$$

$$2(C_6H_5)_2PbCl + 3Hg \longrightarrow 3(C_6H_5)_2Hg + Pb + PbCl_2$$

The reaction between stannous chloride and R_2Hg compounds gave good yields of R_2SnCl_2 derivatives (89).

$$R_2Hg + SnCl_2 \longrightarrow R_2SnCl_2 + Hg$$

This is seen to be exactly the reverse of the reaction above between diphenyllead dichloride and mercury.

The reaction of aluminum with dialkylmercury compounds was used by Buckton and Odling (90a) to prepare trialkylaluminum derivatives. This reaction was further studied by

(87) Gilman and Jones, J. Am. Chem. Soc., 61, 1513 (1939).
(88) Kaplan, Master's Thesis, Iowa State College (1939), p. 49.
(89) (a) Nesmejanow and Kozeschkow, Ber., 63, 2496 (1930).
(b) Eskin, Nesmeyanov and Kocheshkov, J. Gen. Chem. (U.S.S.R.), 8, 35 (1938) /C.A., 32, 5386 (1938)/.
(90) (a) Buckton and Odling, Ann. chim. phys., (4) 4, 492 (1865).
(b) Friedel and Crafts, ibid., (6) 14, 457 (1888).

Friedel and Crafts (90b) who extended it to the preparation of triphenylaluminum. More recently, other workers (91) have found the reaction to be a method of choice for preparing organoaluminum compounds. In boiling xylene solution, diarylmercury derivatives with aluminum gave almost quantitative yields of the R_3Al analogues (92).

Metallic gallium reacts readily with R_2Hg compounds.

$$2Ga + 3R_2Hg \longrightarrow 2R_3Ga + 3Hg$$

By this method good yields of triethylgallium (93) and triphenylgallium (94) have been obtained. In a similar manner, the syntheses of trimethylindium (95) and triphenylindium (38, 96) have been accomplished by heating together metallic indium and the corresponding R_2Hg compounds.

Alkylzinc iodides and powdered tin, when heated at 150 to 160°, were reported to yield R_4Sn compounds (97). Organomercuric chlorides and tin underwent the following transformation

$$2RHgCl + Sn \longrightarrow R_2SnCl_2 + 2Hg$$

If a sodium-tin alloy was used the reaction was represented

(91) (a) Hilpert and Grüttner, Ber., 45, 2828 (1912).
(b) Krause and Dittmar, ibid., 63, 2401 (1930).
(92) Gilman and Marple, Rec. trav. chim., 55, 133 (1936).
(93) Dennis and Patnode, J. Am. Chem. Soc., 54, 182 (1932).
(94) Gilman and Jones, ibid., 62, 980 (1940).
(95) Dennis, Work, Rochow and Chamot, ibid., 56, 1047 (1934).
(96) Gilman and Jones, ibid., 62, 2353 (1940).
(97) Letts and Collie, Phil. Mag., (5) 22, 45 (1886) /Chem. Zentr., 57, 306 (1886)/

as follows (98)

$$2RHgCl + Sn\text{-}Na_2 \longrightarrow R_2Sn + 2Hg + 2NaCl$$

Frankland and Duppa (99) observed a reaction between bismuth and diethylmercury at 120 to 140°, and triethylbismuth was obtained, but the mixture still contained diethylmercury. As mentioned previously, bismuth reacted with diphenylmercury on strong heating but an equilibrium was reached (84), and only about a forty per cent conversion to triphenylbismuth took place. A trace of triphenylbismuth, but mostly diphenylmercury was reported from a reaction of phenylmercuric chloride with sodium-bismuth alloy (100). Tetraphenyllead and bismuth underwent no reaction on heating at 100 to 130° for five hours (101).

Krafft and Lyons (102) have shown that selenium and tellurium react with diarylmercury compounds at high temperatures and are converted to the corresponding R_2Se and R_2Te derivatives.

6. Electrolysis of RM Compounds to Form RM' Compounds.-- The studies of Hein and co-workers (74) on the electrolysis of solutions of ethylsodium in diethylzinc have led to some interesting and significant results. When a lead anode was

(98) Nad and Kocheshkov, J. Gen. Chem. (U.S.S.R.), 8, 42 (1938) /C.A., 32, 5387 (1938)/.
(99) Frankland and Duppa, J. Chem. Soc., 17, 29 (1864).
(100) Zhitkova, Sheverdina and Kocheshkov, J. Gen. Chem. (U.S.S.R.), 8, 1839 (1938) /C.A., 33, 5819 (1939)/.
(101) Gilman and Yablunky, J. Org. Chem., 4, 162 (1939).
(102) Krafft and Lyons, Ber., 27, 1768 (1894).

used one electrochemical equivalent of lead was dissolved from the anode and appeared in the solution as tetraethyllead. In an extension of this work, anodes of other metals were employed (103). The loss in weight of an aluminum electrode was 76 to 87% based on the quantity of current which passed, and triethylaluminum was formed. A magnesium anode was strongly corroded with the production of diethylmagnesium. The loss in weight of various other electrodes, based upon the electrochemical equivalent of current which passed, was 67% for cadmium, 94 to 98% for antimony, and 69% for bismuth. In each case the normal ethyl derivatives of the metals were formed. A thallium electrode was attacked and apparently formed triethylthallium and finely divided thallium metal, probably by way of the reaction

$$3C_2H_5Tl \longrightarrow (C_2H_5)_3Tl + 2Tl$$

the loss in weight of a gold electrode was 1 to 2%, and gold compounds were definitely detected in the solution. Although several forms of the metal were used, tin electrodes were entirely passive, as were also electrodes of copper, iron, platinum, and tantalum.

Kondyrew (104) carried out electrolyses of ethylmagnesium bromide solutions in ether using zinc and aluminum anodes and a platinum cathode. The anodes lost weight

(103) Hein and Segitz, Z. anorg. allgem. Chem., 158, 153 (1926).
(104) Kondyrew, Ber., 58, 459 (1925).

equivalent to the quantity of electricity which passed; presumably diethylzinc and triethylaluminum were formed. Ether solutions of isoamylmagnesium bromide were electrolyzed with a platinum cathode and anodes of various metals (105). Anodes of aluminum, zinc, and cadmium were dissolved as a result of the electrolysis, and in the case of aluminum, the quantity dissolved was approximately equivalent to the current which passed. The products formed were probably organometallic compounds although no search was made for them. Bismuth, gold, nickel, silver, and tin anodes were unattacked.

In these electrolytic processes, free organic radicals are probably produced on the surface of the anode, and they, in turn, may react with the metal of which the anode is made to form RM compounds, as discussed in Section 8. The extensive studies of Evans and co-workers (106) on the electrolysis of Grignard solutions, using inert electrodes, substantiate the view that free radicals are produced during the process.

7. Electrolysis of Ketones to Produce Organolead and Organomercury Compounds.--The preceding section was concerned with electrolysis of organometallic compounds and the formation of new RM derivatives at the anode. Tafel (107) discovered that when methyl ethyl ketone in 30%

(105) French and Drane, J. Am. Chem. Soc., 52, 4904 (1930).
(106) (a) Evans and Field, Ibid., 58, 720, 2284 (1936).
(b) Evans and Braithwaite, ibid., 61, 898 (1939).
(c) Evans, Braithwaite and Field, Ibid., 62, 534 (1940).
(107) Tafel, Ber., 39, 3626 (1906).

sulfuric acid was electrolyzed using a mercury cathode a 20% yield of di-s-butylmercury was produced. A current of 25 amperes at 7.6 to 8.4 volts was used, and the temperature was held at 45 to 50°. The following equation represents the reaction

$$2C_4H_9OH + Hg + 6H^+ \longrightarrow (s\text{-}C_4H_9)_2Hg + 2H_2O$$

Although Tafel and Schmitz (108) had reported earlier that the electrolysis of acetone in aqueous sulfuric acid using a mercury cathode gave isopropyl alcohol, Haggerty (109) reinvestigated this work and found that little alcohol, but mostly diisopropylmercury was produced. Results of duplicate experiments were very erratic, but from some experiments, yields as high as 14% were reported. From the electrolysis of menthone in sulfuric acid-alcohol-water solution, dimenthylmercury has been obtained (110).

The electrolysis of a solution of acetone in 30% aqueous sulfuric acid using a lead cathode gave, besides tetraisopropyllead, low yields of a red-brown oil thought to be diisopropyllead (111). This red oily product was sensitive to air and upon treatment with bromine left diisopropyllead dibromide. When aqueous sulfuric acid solutions of diethyl ketone and methyl ethyl ketone were electrolyzed, red oils

(108) Tafel and Schmitz, Z. Electrochem., 8, 381 (1902) [Chem. Zentr., 73, (1) 1388 (1902)].
(109) Haggerty, Trans. Am. Electrochem. Soc., 56, 421 (1929).
(110) Schall and Kirst, Z. Electrochem., 29, 537 (1923) [Chem. Zentr., 95, (1) 1369 (1924)].
(111) Tafel, Ber., 44, 323 (1911).

were also obtained which appeared to be R_2Pb compounds (112). These materials dissolved in ether and in chloroform and were converted to diamyllead dibromide and di-n-butyllead dibromide, respectively, when treated with bromine.

8. Reactions of Free Radicals with Metals.--Free methyl radicals were said to react readily with the following metals: lithium, sodium, potassium, calcium, zinc, cadmium, mercury, lanthanum, thallium, tin, lead, arsenic, antimony, bismuth, selenium, and tellurium (113). Presumably, CH_3M compounds were formed in each case. From a study of the reaction of free methyl and ethyl radicals on arsenic, antimony, and bismuth, Paneth and Loleit (114) found that compounds of the following types were formed: R_3As, $(R_2As)_2$, $(RAs)_5$, R_3Sb, $(R_2Sb)_2$, R_3Bi, and $(R_2Bi)_2$. An interesting synthesis of trimethylbismuth, probably involving free methyl radicals, was reported to occur when a stream of methane was passed between bismuth electrodes simultaneously with an electric discharge (115).

By the action of sodium on the corresponding free triarylmethyl radicals, Schlenk and Marcus (116) prepared compounds of the type R_3CNa and $RR'R''CNa$. In the presence

(112) Renger, ibid., 44, 337 (1911).
(113) Rice and Rice, "The Aliphatic Free Radicals", The Johns Hopkins Press, Baltimore (1935), p. 58.
(114) Paneth and Loleit, J. Chem. Soc., 366 (1935).
(115) Paneth and Hofeditz, Ber., 62, 1335 (1929).
(116) Schlenk and Marcus, ibid., 47, 1664 (1914).

of a trace of magnesium halide to act as catalyst, magnesium reacted readily with triphenylmethyl, and a quantitative yield of ditriphenylmethylmagnesium resulted (117).

From an extensive study on the decomposition of aryldiazonium chlorides, Waters concluded that free aryl radicals were formed during the process. If certain metals were present during such decompositions, arylmetallic compounds were formed. Thus, aryl $RHgCl$ and R_2SbCl_2 compounds were produced when RN_2Cl compounds were allowed to decompose in the presence of the free metals, calcium carbonate, and acetone (118). Small yields of triphenylarsenic and diphenyltin dichloride were also obtained by this method (119). Earlier workers (120) had already obtained good yields of arylmercuric chlorides by allowing aqueous solutions of aryldiazonium chlorides to decompose in the presence of very finely divided mercury.

Mercury, antimony, and tellurium when heated with diphenyliodonium chloride or di-p-tolyliodonium chloride yielded the corresponding $RHgCl$, R_2Te, and R_3Sb compounds (121). The authors suggested the possibility of a free

(117) (a) Gilman and Fothergill, J. Am. Chem. Soc., 51, 3149 (1929).
(b) Bachmann, ibid., 52, 4413 (1930).
(118) Waters, J. Chem. Soc., 2007 (1937); Makin and Waters, ibid., 843 (1938).
(119) Waters, ibid., 864 (1939).
(120) McClure and Lowy, J. Am. Chem. Soc., 53, 319 (1931).
(121) Sandin, McClure and Irwin, Ibid., 61, 2944 (1939).

radical mechanism.

Nesmejanow and co-workers (122) decomposed double salts of the type $RN_2Cl \cdot SnCl_4$ in hot ethyl acetate in the presence of metallic tin and obtained 5 to 20% yields of R_2SnCl_2 compounds. Good yields of RHgCl compounds resulted when diazonium fluoride-boron fluoride complexes, RN_2BF_4, were decomposed in water-acetone solutions of $HgCl_2$ in the presence of finely divided mercury (123). The mechanisms of these reactions are not well understood but perhaps, as Waters (119) believes, free radicals take part. Closely related reactions of diazonium compounds will be discussed in a later section.

9. The Addition of Metals to Double Bonds.--The addition to carbon-carbon, carbon-nitrogen and carbon-oxygen double bonds is apparently characteristic only of the alkali metals. The first systematic study (124) of these addition reactions was reported in 1914. It was shown that sodium reacts with a variety of compounds containing carbon-carbon double bonds. For example, stilbene with sodium gave the compound, $C_6H_5CHNaCHNaC_6H_5$. The C=N bond, as in benzophenone-anil, adds sodium to form compounds of the type $R_2C(Na)N(Na)R$, and from aromatic ketones, such as benzophenone,

(122) Nesmejanow, Kozeschkow and Klimowa, Ber., 68, 1877 (1935).
(123) Dunker, Starkey and Jenkins, J. Am. Chem. Soc., 58, 2308 (1936).
(124) Schlenk, Appendrodt, Michael and Thal, Ber., 47, 473 (1914).

the ketyls are obtained.

$$(C_6H_5)_2C{=}O + Na \longrightarrow (C_6H_5)_2C(Na)ONa$$

Our knowledge of these addition reactions of sodium and lithium to compounds containing double bonds has been greatly extended by the studies of Schlenk and Bergmann (125). The facility with which sodium adds to naphthalene has been greatly increased by using dimethyl ether as a solvent; and in this solvent it has been found that sodium will even add to biphenyl (126).

10. The Cleavage of Carbon-Carbon Bonds by Alkali Metals.--Certain hydrocarbons having weak carbon-carbon bonds are split by alkali metals with the formation of two organometallic molecules.

$$2M + R{-}R' \longrightarrow RM + R'M$$

The following reaction is an example of this with a hydrogen displacement (Section 3) taking place at the same time (127).

$$(C_6H_5)_2C{-}CH{=}C(C_6H_5)_2 + Li \longrightarrow$$
$$(C_6H_5)_2CLi + (C_6H_5)_2C(Li)\underset{H}{C}{=}\underset{H}{C}C(Li)(C_6H_5)_2$$

Sodium-potassium alloy, acting on symmetrical tetraphenylethane, cleaved the latter and yielded two molecules of diphenylmethylpotassium (49). Conant and Garvey (128) have

(125) Schlenk and Bergmann, Ann., 463, 1, 228 (1928); 464, 22 (1928); 479, 42, 58, 78 (1930).
(126) Scott, Walker and Hansley, J. Am. Chem. Soc., 58, 2442 (1936).
(127) Koelsch and Rosenwald, ibid., 59, 2170 (1937).
(128) Conant and Garvey, ibid., 49, 2599 (1927).

studied the cleavage of a series of variously substituted ethanes using sodium-potassium alloy and sodium amalgam. Marvel and co-workers (129) made a similar study on a large series of phenylethynyl- and t-butylethynylethanes.

II. Preparations of Organometallic Compounds from Salts of the Metals

1. Reactions of Organometallic Compounds with Salts of Other Metals.—The reactions represented by the type equation, $RM + M'X \rightleftharpoons RM' + MX$, have been, by far, the most widely used to prepare all types of organometallic compounds. Because of the ease of obtaining a large variety of Grignard reagents, and because of their comparatively high reactivity, these reagents have been particularly useful in preparing a great many less reactive organometallic compounds. They have largely filled the position formerly occupied by organozinc compounds. As indicated in the equation, these reactions are probably essentially reversible, although in many cases this reversibility has not been demonstrated.

Reich (130) reported the first preparation of an organocopper compound by the reaction of phenylmagnesium

(129) Salzberg and Marvel, J. Am. Chem. Soc., 50, 1737, 2840 (1928); Rossander and Marvel, ibid., 51, 932 (1929); Stampfli and Marvel, ibid., 53, 4057 (1931); Gillespie and Marvel, ibid., 52, 3368 (1930).
(130) Reich, Compt. rend., 177, 322 (1923).

bromide with cuprous iodide. In the same way, Reich, as well as other workers (131), prepared phenylsilver from silver bromide and phenylmagnesium bromide. Earlier, Krause and Schmitz (132) had obtained the interesting compound, $C_6H_5Ag \cdot AgNO_3$, from the reaction of silver nitrate with triphenylethyllead and triphenylethyltin. The closely related aryl R_4Pb and R_4Sn derivatives did not react with silver nitrate. Organobismuth compounds were said to react with alcoholic silver nitrate to give yellow precipitates which were thought to be organosilver compounds (133).

Diethylgold bromide (134) was prepared in low yields from ethylmagnesium bromide and auric chloride. Kharasch and Isbell (135) prepared several other alkyl gold compounds by this method. Arylgold compounds were not formed in the reactions of aryl Grignard reagents with gold chloride. More recently, dimethylgold iodide has been obtained (136).

Ninety per cent yields of dimethylberyllium and good yields of other R_2Be compounds have been prepared from beryllium chloride and Grignard reagents (79). Ether solutions of diphenylberyllium were easily obtained from beryllium chloride and phenylmagnesium bromide (137).

(131) Krause and Wendt, Ber., 56, 2064 (1923); Gilman and Straley, Rec. trav. chim., 55, 821 (1936).
(132) Krause and Schmitz, Ber., 52, 2159 (1919).
(133) Challenger and Allpress, J. Chem. Soc., 119, 913 (1921).
(134) Pope and Gibson, ibid., 91, 2061 (1907).
(135) Kharasch and Isbell, J. Am. Chem. Soc., 53, 2701 (1931).
(136) Brain and Gibson, J. Chem. Soc., 762 (1939).
(137) Gilman and Baillie, J. Org. Chem., 2, 84 (1937).

The reverse of the reaction between silver bromide and phenylmagnesium bromide, to give phenylsilver, was reported by Bickley and Gardner (138) who obtained phenylmagnesium iodide from phenylsilver and magnesium iodide in ether.

$$C_6H_5Ag + MgI_2 \longrightarrow C_6H_5MgI + AgI$$

A magnesium halide can apparently be easily and completely converted to a Grignard reagent in ether solution by the action of an organolithium compound (139).

$$RLi + MgX_2 \longrightarrow RMgX + LiX$$

Ether solutions of R_2Zn compounds are readily made by the interaction of Grignard reagents with zinc halides (140). Krause and Fromm (141) have used the following reaction for the preparation of unsymmetrical organozinc compounds

$$RZnX + R'MgX \longrightarrow RZnR' + MgX_2$$

Although organocadmium compounds are difficult to obtain otherwise, they may be synthesized in good yields from Grignard reagents and cadmium halides (142). Cadmium chloride appears to be the best halide to use for this purpose (143).

Some of the early workers on organomercury compounds

(138) Bickley and Gardner, Ibid., 5, 126 (1940).
(139) Gilman and Swiss, J. Am. Chem. Soc., 62, 1847 (1940).
(140) Ref. 18, p. 115.
(141) Krause and Fromm, Ber., 59, 931 (1926).
(142) Krause, Ibid., 50, 1813 (1917).
(143) Gilman and Nelson, Rec. trav. chim., 55, 518 (1936).

prepared them from R_2Zn derivatives and mercuric chloride (144). Pfeiffer and Truskier (145) were the first to employ the Grignard reagent for the synthesis of R_2Hg derivatives from mercuric chloride. Phenylboric acid and mercuric chloride reacted immediately in aqueous solution and yielded phenylmercuric chloride (146). This is the reverse of a reaction, to be mentioned shortly, for preparing RBX_2 compounds from the R_2Hg analogues. The reaction

$$RHgX + ArB(OH)_2 + NaOH \longrightarrow RHgAr$$

has found use as a method for making unsymmetrical organomercury compounds (147). In place of arylboric acids, diaryltin dichlorides or diarylantimony chlorides may be used. The analogous reaction between diaryltin dihalides and mercuric chloride gave high yields of diarylmercurials (132). These reactions between tin and mercury compounds are reversible as will be seen later. Phenylmercuric chloride was produced by the reaction of mercuric chloride with either triphenylethyllead or triphenylethyltin in alcohol (132). Recently, it was shown that mercuric chloride reacted with

(144) (a) Buckton, Ann., 109, 218 (1859).
(b) Frankland, Ibid., 111, 44 (1859).
(145) Pfeiffer and Truskier, Ber., 37, 1125 (1904). See also ref. 84 and Marvel and Calvery, J. Am. Chem. Soc., 45, 820 (1923).
(146) (a) Michaelis and Becker, Ber., 15, 180 (1882).
(b) Khotinsky and Melamed, Ibid., 42, 3090 (1909).
(147) Freidlina, Nesmejanow and Kozeschkow, Ibid., 68, 565 (1935).
(148) Morton, Massengale and Gibb, J. Am. Chem. Soc., 63, 324 (1941).

n-amylsodium in petroleum ether, and a good yield of di-n-amylmercury resulted (148).

Reactions of halides of the third group elements with other RM compounds have been used to obtain organometallic derivatives of boron, aluminum, gallium, and thallium. Pure samples of trimethylboron and triethylboron were prepared by the reaction of boron chloride and the R_2Zn compounds (149). Much earlier, Frankland and Duppa (150) had used this same reaction employing boron chloride and also ethyl orthoborate. Khotinsky and Melamed (146b) applied the reaction of Grignard reagents with boric acid esters to synthesize a series of organoboric acids of the type $RB(OH)_2$. This reaction has more recently been investigated by Johnson and co-workers (151) who obtained tri-n-butylboron.

$$n\text{-}C_4H_9MgBr + B(OCH_3)_3 \longrightarrow (n\text{-}C_4H_9)_3B$$

A superior method for the synthesis of R_3B compounds is the reaction of Grignard reagents on boron fluoride-etherate (152). The extensive studies by Michaelis (153) on the reactions of boron chloride or boron bromide with diarylmercury compounds have shown that either RBX_2 or R_2BX types can be formed depending upon the quantity of R_2Hg compound used.

(149) Stock and Zeidler, Ber., 54, 531 (1921).
(150) Frankland and Duppa, Ann., 115, 319 (1860).
(151) Johnson, Snyder and Van Campen, J. Am. Chem. Soc., 60, 115 (1938).
(152) Krause and Nitsche, Ber., 54, 2784 (1921).
(153) Michaelis, ibid., 27, 244 (1894); Ann., 315, 29 (1901).

Stable etherates of organoaluminum compounds are formed by the reaction of Grignard reagents with aluminum halides (154).

$$3RMgX + AlX_3 + (C_2H_5)_2O \longrightarrow R_3Al\cdot(C_2H_5)_2O + 3MgX_2$$

Aluminum chloride has been reported (155) to react with organosilicon compounds and yield silicon tetrachloride together with aluminum derivatives of the type $RAlCl_2$. Some interesting reactions between tetraphenyllead or triphenyllead chloride and aluminum chloride gave phenylaluminum dichloride as one of the products (156). Tetraethyllead and aluminum chloride produced $C_2H_5AlCl_2$, $(C_2H_5)_2AlCl$, and a little $(C_2H_5)_3Al$.

The reaction of ethylmagnesium bromide with gallium bromide was used to prepare the first organogallium compound (93). The product was an etherate of the formula, $(C_2H_5)_3Ga\cdot(C_2H_5)_2O$. Dimethylgallium etherate was obtained in a 90% yield by the same method (157). The reaction between gallium bromide and dimethylzinc was said to give a quantitative yield of trimethylgallium (157b).

The only means by which organothallium compounds have been prepared is through the reaction of a thallium salt

(154) Krause and Wendt, Ber., 56, 466 (1923).
(155) Evison and Kipping, J. Chem. Soc., 2774 (1931).
(156) Gilman and Apperson, J. Org. Chem., 4, 162 (1939).
(157) (a) Renwanz, Ber., 65, 1308 (1932).
(b) Kraus and Toonder, Proc. Natl. Acad. Sci., 19, 292 (1933) /C.A., 27, 2646 (1933)/.

with another RM compound. Hansen (158), who first investigated the reaction of thallic chloride with diethylzinc in ether solution, thought he obtained triethylthallium, and possibly he did. The triethylthallium, however, could not be separated, so the mixture was decomposed to give the highly stable diethylthallium chloride. Other investigators (159) believed that the reaction of diethylzinc and thallic chloride proceeded only to the diethylthallium chloride stage and that no triethylthallium was formed. Meyer and Bertheim (160) used Grignard reagents with thallic chloride to obtain compounds of the type R_2TlX. Later workers (161) have prepared a large number of R_2TlX compounds through the Grignard reaction. Goddard (161a) has reacted thallic chloride with several other RM compounds. For example, R_2TlX derivatives were obtained, often in good yields from R_4Sn, R_3Bi, $(C_6H_5)_2Hg$, $(C_3H_7)_2Hg$, $(C_6H_5)_4Pb$, $(C_2H_5)_2(C_6H_5)_2Pb$, and others. The R_3Sb and R_3P compounds and some derivatives of mercury and lead gave only thallous chloride. A smooth reaction takes place between thallic halides and arylboric acids in water solution, and either R_2TlX or $RTlX_2$ types may be obtained depending upon the ratio of the reactants (162). This

(158) Hansen, Ber., 3, 9 (1870).
(159) Hartwig, Ibid., 7, 298 (1874).
(160) Meyer and Bertheim, ibid., 37, 2051 (1904).
(161) (a) Goddard, J. Chem. Soc., 121, 36, 356, 482 (1922); 123, 1161 (1923).
(b) Krause and v. Grosse, Ber., 58, 1933 (1925).
(162) Challenger and Parker, J. Chem. Soc., 1463 (1931).

method has been used to obtain a variety of substituted diarylthallium halides (163). The only R_2Tl compounds which have been isolated were prepared through the reaction (87, 164)

$$R_2TlBr + RLi \longrightarrow R_2Tl + LiBr$$

Menzies and Cope (165) carried out reactions of thallous bromide and also thallous ethoxide with ethylmagnesium bromide and found that the reaction may be represented by the following equation

$$3C_2H_5MgBr + 3TlOC_2H_5 \longrightarrow (C_2H_5)_2Tl + 2Tl + 3MgX_2$$

Phenyllithium (164b, 166) and also methyllithium (167) have been shown to give a similar reaction with thallous halides.

In the fourth group, organometallic compounds of silicon, germanium, tin, and lead have been prepared by allowing halides of these elements to react with other organometallic compounds. In 1865, Friedel and Crafts (168) obtained tetramethylsilicon by heating silicon tetrachloride with dimethylzinc in a sealed tube. Dimethylzinc has also been used to prepare the methylsilanes, CH_3SiH_3 and $(CH_3)_2SiH_2$, from the corresponding chloro-

(163) Melnikov and Rokitskaya, J. Gen. Chem. (U.S.S.R.), 7, 1472 (1937) /C.A., 32, 127 (1938)/.
(164) (a) Grell, J. Am. Chem. Soc., 52, 2998 (1930).
(b) Birch, J. Chem. Soc., 1132 (1934).
(165) Menzies and Cope, J. Chem. Soc., 2862 (1932).
(166) Gilman and Jones, J. Am. Chem. Soc., 62, 2357 (1940).
(167) Unpublished study by the author.
(168) Friedel and Crafts, Ann., 136, 203 (1865).

silanes (169). Kipping (170) made compounds of the type R_4Si, R_3SiCl, and R_2SiCl_2 by reactions of Grignard reagents with silicon tetrachloride. Schumb and co-workers (171) obtained $R_3Si-SiR_3$ and $R_3Si-O-SiR_3$ compounds from reactions of Grignard reagents (171a) and organosodium compounds (171b) with the halides, $Cl_3Si-SiCl_3$ and $(Cl_3Si)_2O$. Diarylmercury compounds and silicon tetrachloride have given products of the type R_2SiCl_2 (172). Esters such as methyl or ethyl orthosilicate react as do the halides. Thus, from these esters and a mixture of diethylzinc and sodium, Ladenburg (172) prepared $(C_2H_5)_2Si(OR)_2$ derivatives. Acids of the type RSiOOH were obtained from aryl Grignard reagents and ethyl orthosilicate (173). Recently, a 21% yield of tetrabenzylsilicon has been reported from the reaction of benzylmagnesium chloride with sodium fluorosilicate at high temperatures (174).

Soon after the discovery of germanium, Winkler (175) synthesized the tetraethyl derivative by the action of diethylzinc on germanium tetrachloride. The R_2Zn compounds have also been used by other workers to prepare tetraethyl-

(169) Stock and Somieski, Ber., 52, 695 (1919).
(170) Kipping, Proc. Chem. Soc., 20, 15 (1904) /Chem. Zentr., 75, (1) 636 (1904)/.
(171) (a) Schumb and Saffer, J. Am. Chem. Soc., 61, 363 (1939).
(b) Schumb and Saffer, Ibid., 63, 93 (1941).
(172) Ladenburg, Ann., 164, 300 (1872); 173, 143 (1874).
(173) Khotinsky and Seregenkoff, Ber., 41, 2946 (1908).
(174) Soschestvenskaya, J. Gen. Chem. (U.S.S.R.), 8, 297 (1938) /C.A., 32, 5391 (1938)/.
(175) Winkler, J. prakt. Chem., 36, 177 (1887).

germanium (22) and tetraphenylgermanium (176) in good yields. Although alkylmagnesium halides react with germanium tetrachloride to give good yields of R_4Ge derivatives (177, 178), it has been repeatedly observed (22, 177, 179, 180) that certain other Grignard reagents give mostly R_3GeX, R_2GeX_2, and $RGeX_3$ compounds and very little of the R_4Ge derivative even when a large excess of the Grignard reagent is used. Worral (181), however, found, in the case of the phenyl compound at least, that it was only necessary to replace the ether of the reaction mixture with toluene and reflux a short time in order to obtain an 86% yield of tetraphenylgermanium from germanium tetrachloride and phenylmagnesium bromide. No excess of the Grignard reagent was necessary. Germanium tetrachloride reacted with diarylmercury compounds (178, 180), and, after hydrolysis of the reaction mixtures, products of the formula $(RGeO)_2O$ were isolated.

The various kinds of organotin compounds, R_4Sn, R_3SnX, R_2SnX_2, and $RSnX_3$, were synthesized from stannic halides and Grignard reagents in 1904 (182). Organolithium compounds may sometimes be used to advantage in preparing R_4Sn deriva-

(176) Kraus and Foster, J. Am. Chem. Soc., 49, 457 (1927).
(177) Tabern, Orndorff and Dennis, ibid., 47, 3039 (1925).
(178) Orndorff, Tabern and Dennis, ibid., 49, 2512 (1927).
(179) Morgan and Drew, J. Chem. Soc., 127, 1760 (1925).
(180) Bauer and Burschkies, Ber., 65, 956 (1932).
(181) Worrall, J. Am. Chem. Soc., 62, 3267 (1940).
(182) (a) Pope and Peachy, Proc. Chem. Soc., 19, 290 (1903) /Chem. Zentr., 75, (1) 353 (1904)/.
(b) Pfeiffer and Schnurmann, Ber., 37, 319 (1904).

tives as shown in the synthesis of tetra-p-dimethylaminophenyltin from stannic chloride and p-dimethylaminophenyllithium (183). Frankland and Lawrance (184) used diethylzinc to prepare tetraethyltin from stannic chloride. Diphenylmercury and stannic chloride were found to produce diphenyltin dichloride (185). In a very similar way, diphenyltin dichloride has been obtained from reactions of stannic chloride with triphenylbismuth (186) and tetraphenyllead (187). A common reaction of organometallic compounds with halides of the same metal is illustrated in the reaction of stannic chloride with tetraphenyltin to give two molecules of diphenyltin dichloride (187).

$$SnCl_4 + (C_6H_5)_4Sn \longrightarrow 2(C_6H_5)_2SnCl_2$$

Reactions of Grignard reagents with stannous halides have given the more or less stable R_2Sn derivatives. Pfeiffer (188a) reported the preparation of an impure sample of diethyltin from ethylmagnesium bromide and stannous chloride. Diaryltin compounds, stable enough to be recrystallized and handled in the air, were prepared from Grignard reagents and stannous chloride (188b).

As early as 1861, Buckton (144a) prepared tetraethyllead

(183) Austin, J. Am. Chem. Soc., 54, 3726 (1932).
(184) Frankland and Lawrance, J. Chem. Soc., 35, 130 (1879).
(185) Aronheim, Ann., 194, 145 (1878).
(186) Challenger and Pritchard, J. Chem. Soc., 125, 864 (1924).
(187) Goddard, Ashley and Evans, ibid., 121, 978 (1922).
(188) (a) Pfeiffer, Ber., 44, 1269 (1911).
(b) Krause and Becker, ibid., 53, 173 (1920).

by heating lead chloride with diethylzinc. Later workers have reported 90% yields of tetraethyllead from this reaction (189). Pfeiffer and Truskier (145) were the first to use Grignard reagents to prepare R_4Pb compounds from lead chloride. This reaction is a superior method for obtaining such compounds (190). In the reaction of Grignard reagents, organozinc compounds, organolithium compounds, and other RM compounds with lead halides (PbX_2), metallic lead is always one of the products. The over-all process may be represented by the equation (145)

$$4RM + 2PbX_2 \longrightarrow R_4Pb + Pb + 4MX$$

The reaction mechanism is, however, by no means clear. Under proper conditions, $(R_2Pb)_2$ compounds may be the chief products (191). Possibly R_2Pb derivatives are first formed, for some of these (191a) have actually been isolated in small quantities from the reaction of arylmagnesium halides with lead chloride at low temperatures. Diphenyllead dichloride and diphenylmercury , heated in pyridine, reacted to give only a fair yield of triphenyllead chloride (192).

$$(C_6H_5)_2PbCl_2 + (C_6H_5)_2Hg \longrightarrow (C_6H_5)_3PbCl + C_6H_5HgCl$$

(189) Meyer, Chem. News, 131, 1 (1925) [C.A., 19, 2636 (1925)].
(190) Grüttner and Krause, Ber., 49, 1415 (1916).
(191) (a) Krause and Reissaus, ibid., 55, 888 (1922).
(b) Krause and Schlöttig, ibid., 58, 427 (1925).
(c) Calingaert and Soroos, J. Org. Chem., 2, 535 (1938).
(d) Gilman and Baillie, J. Am. Chem. Soc., 61, 731 (1939).
(192) Austin, J. Am. Chem. Soc., 54, 3387 (1932).

Arsenic trichloride and R_2Zn compounds react to give good yields of aliphatic R_3As derivatives (193); but the best and easiest method for preparing organoarsenic compounds from arsenic trihalides is probably through the Grignard reagents (194). Strangely enough, arsenous oxide also reacts readily with Grignard reagents (195), and good yields of triarylarsenic types have been obtained from this reaction. Tetraphenyllead and arsenic trichloride reacted in hot toluene and gave a 91% yield of diphenylarsenic chloride (196).

$$(C_6H_5)_4Pb + AsCl_3 \longrightarrow (C_6H_5)_2PbCl_2 + (C_6H_5)_2AsCl$$

A mixture containing diphenylbismuth chloride, diphenylarsenic chloride, and phenylarsenic dichloride was obtained from a reaction of triphenylbismuth with arsenic trichloride (196).

Organoantimony compounds, like those of arsenic, are best prepared from antimony trichloride and Grignard reagents (194a, 194b, 197). Buckton (198) reported that diethylmercury and antimony trichloride gave triethylantimony. Diphenylmercury, in a reaction with antimony trichloride, gave both

(193) (a) Cahours and Hofmann, Compt. rend., 41, 831 (1855).
(b) Hofmann, Ann., 103, 357 (1857).
(c) Renshaw and Holm, J. Am. Chem. Soc., 43, 1468 (1920).
(194) (a) Pfeiffer, Ber., 37, 4620 (1904).
(b) Hibbert, ibid., 39, 160 (1906).
(c) Seifter, J. Am. Chem. Soc., 61, 530 (1939).
(195) (a) Sachs and Kantorowicz, Ber., 41, 2767 (1908).
(b) Blicke and Smith, J. Am. Chem. Soc., 51, 1558 (1929).
(196) Challenger and Ridgway, J. Chem. Soc., 121, 104 (1922).
(197) (a) Dyke, Davies and Jones, Ibid., 463 (1930).
(b) Grüttner and Wiernik, Ber., 48, 1749, 1759 (1915).
(198) Buckton, J. Chem. Soc., 16, 22 (1863).

triphenylantimony dichloride and diphenylantimony trichloride (196). Tetraphenyllead and antimony trichloride have given a 92% yield of diphenylantimony chloride (187). Antimony trichloride with triphenylbismuth yielded triphenylantimony dichloride (196). Triethylantimony diiodide was the product from a reaction of antimony pentachloride with ethylmagnesium iodide (182b); and diphenylantimony trichloride was obtained from tetraphenyllead with antimony pentachloride (187). Amorphous antimony sulfide, Sb_2S_3, reacted with α-naphthylmagnesium bromide and gave a small quantity of tri-α-naphthylantimony (199). A similar reaction with antimony oxide yielded no organoantimony compounds.

The reaction of Grignard reagents with bismuth halides, initiated by Pfeiffer (194a), has been widely used to synthesize a great number of organobismuth compounds (196, 200). The older method using R_2Zn compounds with bismuth halides also apparently gave satisfactory yields of R_3Bi derivatives (201). Challenger and Allpress (133) reported a quantitative yield of triphenylbismuth from the reaction

$$(C_6H_5)_2Hg + BiBr_3 \longrightarrow (C_6H_5)_3Bi + HgBr_2$$

Later it was shown that the reaction is actually reversible, and from triphenylbismuth and mercuric chloride, phenylmercuric

(199) Matsumiya, Mem. College Sci. Kyoto Imp., 8, 11 (1925) /C.A., 19, 1704 (1925)/.
(200) (a) Challenger, J. Chem. Soc., 105, 2310 (1914).
(b) Krause and Renwanz, Ber., 65, 777 (1932).
(c) Gilman and Yablunky, J. Am. Chem. Soc., 63, 207 (1941).
(201) (a) Marquardt, Ber., 20, 1516 (1887).
(b) Marquardt, Ibid., 21, 2035 (1888).

chloride and diphenylbismuth chloride resulted (196). Bismuth bromide and tetraphenyllead produced diphenylbismuth bromide (187); but bismuth chloride and tetraethyllead gave triethylbismuth as well as diethylbismuth chloride (156) A solution of bismuth bromide and triphenylbismuth in ether yielded diphenylbismuth bromide (197).

The researches of Hein and co-workers (202) on the reaction of Grignard reagents with chromium salts have led to the discovery of the organochromium compounds. For example, phenylmagnesium bromide and chromic chloride reacted to yield a mixture of the three substances, $(C_6H_5)_3CrBr$, $(C_6H_5)_4CrBr$, and $(C_6H_5)_2CrBr$. Apparently, chromium in the form of a non-ionized salt is necessary if organochromium compounds are to be obtained (203). Molybdenum pentachloride, molybdenum trichloride, and molybdenum tribromide were said to react with phenylmagnesium bromide and give organomolybdenum compounds analogous with those of chromium (204). Recently, organotungsten compounds have been reported from the reaction of phenylmagnesium bromide with tungsten hexachloride or hexaphenoxide (205).

Organoselenium compounds may be prepared by means of the Grignard reagent. An example is the synthesis of unsymmetrical

(202) (a) Hein, ibid., 54, 1905 (1921).
(b) Hein and Späte, ibid., 57, 899 (1924).
(c) Hein, Reschke and Pintus, ibid., 60, 749 (1927).
(203) Hein, J. prakt. Chem., 153, 160 (1939).
(204) Hein, Angew. Chem., 51, 503 (1938).
(205) Hein and Nebe, Naturwissenschaften, 28, 93 (1940).

derivatives (206) through the reaction

$$RSeBr + R'MgX \longrightarrow RSeR' + MgXBr$$

Leicester (207) found that selenium tetrabromide reacted with diarylmercury compounds or arylmercuric halides to give quantitative yields of R_2Se derivatives.

$$3RHgBr + SeBr_4 \longrightarrow R_2Se + HgBr_2 + RBr$$

Tellurium tetrachloride heated with tetraphenyllead in toluene produced a 50% yield of diphenyltellurium dichloride (187). Lederer (208) has reacted tellurium tetrabromide and tetrachloride with aryl Grignard reagents and obtained a large number of diaryltellurides (208a) and triaryltellurium halides (208b).

There seems to be good evidence that phenylmagnesium iodide reacts with manganese iodide to form an organomanganese compound (209). This product, however, has never been isolated in a pure state.

Platinic chloride and methylmagnesium iodide yielded trimethylplatinum iodide (210). It was later shown that this reaction also gave tetramethylplatinum (211). The latter compound was obtained in a 46% yield by the action of methylsodium on trimethylplatinum iodide (211).

(206) Behaghel and Siebert, Ber., 66, 708 (1933).
(207) Leicester, J. Am. Chem. Soc., 60, 619 (1938).
(208) (a) Lederer, Ber., 47, 277 (1914); 49, 1071, 2532 (1916).
(b) Lederer, Ibid., 44, 2287 (1911); 48, 1944 (1915).
(209) Unpublished studies by E. Bindschadler.
(210) Pope and Peachey, J. Chem. Soc., 95, 571 (1909).
(211) Gilman and Lichtenwalter, J. Am. Chem. Soc., 60, 3085 (1938).

Before leaving this section it will be well to point out, again, those cases in which inorganic compounds other than halides have been converted to organometallic compounds by means of Grignard reagents. Reactions of boric acid esters, $B(OR)_3$, with Grignard reagents produced $RB(OH)_2$ (146b) and R_3B compounds (151). Thallous ethoxide and ethylmagnesium bromide gave triethylthallium as one product (165). Esters of silicic acid, $Si(OR)_4$, reacted with R_2Zn compounds to give $R_2Si(OR)_2$ derivatives (172), and with Grignard reagents to give $RSiOOH$ acids (173). The reaction of arsenous oxide with Grignard reagents has been reported as a good method for preparing triarylarsenic compounds (195). Antimony sulfide reacted with α-naphthylmagnesium bromide to give tri-α-naphthylantimony (199). Finally, the preparation of organotungsten compounds from tungsten hexaphenoxide and phenylmagnesium bromide has been claimed (205).

3. Reactions of Lower Valent Metal Halides with RM Compounds in the Presence of Organic Halides (212).--In the preceding section it was mentioned that the reaction of a Grignard reagent or an organolithium compound with a thallous halide immediately produced metallic thallium and an R_3Tl compound (167). A similar reaction with lead halides was also pointed out (145).

$$2PbX_2 + 4RM \longrightarrow R_4Pb + Pb + 4MX$$

(212) Unpublished studies by the author.

The free metals so formed are in a state of very fine subdivision and they appear to react readily with organic halides, although ordinary forms of these metals do not react with such halides.

When an RLi compound is added to a suspension of a thallous halide in an ether solution containing an organic iodide, the following sequence of transformations takes place

$$3RLi + 3TlX \longrightarrow R_3Tl + 2Tl + 3LiX$$

$$3RI + 2Tl \longrightarrow R_2TlI + RTlI_2$$

$$R_2TlI + RTlI_2 + 3RLi \longrightarrow 2R_3Tl + 3LiI$$

If these three equations are added, the over-all reaction is seen to be

$$2RLi + TlX + RI \longrightarrow R_3Tl + LiX + LiI$$

The reaction of thallous iodide, methyllithium, and methyl iodide gave a 90% yield of trimethylthallium; and from thallous chloride, phenyllithium and iodobenzene an 80% yield of triphenylthallium was obtained.

Reactions of lead halides with Grignard reagents and organolithium compounds in the presence of organic iodides can be represented by the equations

$$4RM + 2PbX_2 \longrightarrow R_4Pb + Pb + 4MX$$

$$2RI + Pb \longrightarrow R_2PbI_2$$

$$R_2PbI_2 + 2RM \longrightarrow R_4Pb + 2MX + MI$$

Addition of these equations gives the total reaction

$$3RM + PbX_2 + RI \longrightarrow R_4Pb + 2MX + MI$$

A quantitative yield of tetramethyllead was obtained from

methyllithium, lead iodide, and methyl iodide; and from methylmagnesium chloride, lead chloride, and methyl iodide the yield of tetramethyllead was in excess of 70%. Reactions of phenyllithium, lead chloride, and iodobenzene gave excellent yields of tetraphenyllead, based on the above equation (213).

The lower valent halides of mercury, germanium, and tin might be expected to undergo reactions similar to the above reactions of thallous and lead halides.

3. Reactions of Metal Halides with Organic Halides Using Sodium as a Condensing Agent.--The familar "Wurtz" type of condensation exemplified in the reaction

$$2RX + 2Na \longrightarrow R\text{-}R + 2NaX$$

has been applied to the condensation of inorganic halides with organic halides. Polis (214) obtained R_4Si compounds (where R = phenyl, p-tolyl, and benzyl) from reactions of the organic halides and silicon tetrachloride with sodium in ether.

$$SiCl_4 + 4RX + 8Na \longrightarrow R_4Si + 8NaX$$

A little ethyl acetate was used to catalyze the reactions. Kipping and Lloyd (215) prepared aliphatic R_4Si derivatives by this same method. The chloride, $Cl_3Si\text{-}SiCl_3$, with chlorobenzene and sodium was cleaved and gave tetraphenylsilicon

(213) Studies by R. W. Leeper.
(214) Polis, Ber., 18, 1540 (1885).
(215) Kipping and Lloyd, J. Chem. Soc., 79, 449 (1901).

rather than the expected disilane (216).

Tetraphenylgermanium and tetra-p-tolylgermanium were made through the reaction of the aryl bromides, germanium tetrachloride, and sodium in ether (177). An improvement in the yield of tetraphenylgermanium was claimed when the reaction was carried out in toluene (181).

Contrary to the report of Polis (57), tetraphenyltin can, apparently, be prepared in good yields from the reaction of stannic chloride, bromobenzene, and sodium in ether solution (177).

One of the best methods of preparing aryl R_3As and R_3Sb compounds seems to be the reaction of the trihalides of the metals with aryl chlorides and sodium (217).

$$SbCl_3 + 3C_6H_5Cl + 6Na \longrightarrow (C_6H_5)_3Sb + 6NaCl$$

Tri-n-propylarsenic has been made from arsenic trichloride, n-propyl chloride, and sodium (218).

4. The Addition of Organic Halides to Some Metallic Salts.--The reaction expressed in the equation

$$MX_2 + RI \longrightarrow RMX_2$$

has been found applicable to the preparation of organometallic compounds of germanium, tin, and lead. A mixture of ethyl iodide and germanium diiodide heated at 110° in a sealed tube

(216) Schumb, Ackerman and Saffer, J. Am. Chem. Soc., 60, 2486 (1938).
(217) Michaelis and Reese, Ber., 15, 2876 (1882); Ann., 233, 39 (1886); Michaelis, Ibid., 321, 160 (1902); Morgan and Vining, J. Chem. Soc., 117, 777 (1920).
(218) Dehn, Am. Chem. J., 40, 115 (1908).

for three days has been reported to give an almost quantitative yield of ethylgermanium triiodide (219).

$$GeI_2 + C_2H_5I \longrightarrow C_2H_5GeI_3$$

A reaction probably of this same nature, although the mechanism is not well understood, is that between alkyl or aryl iodides and the salt, $CsGeCl_3$ (220).

$$CsGeCl_3 + RI \longrightarrow RGeCl_3 + CsI$$

Good yields of ethylgermanium trichloride and phenylgermanium trichloride were reported.

Stannous iodide and methyl iodide were found to react smoothly when heated together, and the product was methyltin triiodide (221). Closely related reactions of alkyl iodides with a potassium chloride-stannous chloride double salt have been carried out in sealed tubes which were heated at about 100° for forty-eight hours (222). A 44% yield of methyltin triiodide was obtained when methyl iodide was used. The mechanism of the reaction was pictured as follows

$$KSnCl_3 + CH_3I \longrightarrow KI + CH_3SnCl_3$$

$$CH_3SnCl_3 + 3KI \longrightarrow CH_3SnI_3 + 3KCl$$

An alternative process would be

$$KSnCl_3 + 2KI \longrightarrow SnI_2 + 3KCl$$

$$SnI_2 + CH_3I \longrightarrow CH_3SnI_3$$

and this seems especially probable since the second step

(219) Flood, J. Am. Chem. Soc., 55, 4935 (1933).
(220) Tchakirian and Lewinsohn, Compt. rend., 201, 835 (1935).
(221) Pfeiffer and Heller, Ber., 37, 4618 (1904).
(222) Tchakirian, Lesbre and Lewinsohn, Compt. rend., 202, 138 (1936).

in this mechanism is a reaction already known to take place (221). From the reaction of i-propyl iodide with $KSnCl_3$, however, the compound, i-$C_3H_7SnCl_3$, was actually isolated in a 40% yield, and this points to the first mechanism as most likely. The reactions of the potassium chloride-stannous chloride double salt are related closely to a reaction of methyl iodide with stannic oxide in basic aqueous alcohol solution. This process, first used by Meyer (223), led to the formation of methylstannic acid.

$$CH_3I + SnO_2 + OH^- \longrightarrow CH_3SnOOH$$

Pfeiffer (224) later studied the reaction using a series of alkyl iodides.

$$SnO_2K_2 + RI \longrightarrow RSnO_2K + KI$$

$$2RSnO_2K \longrightarrow R_2SnO + K_2SnO_3$$

Although the potassium chloride-lead chloride salt, $KPbCl_3$, did not react with alkyl iodides, the compound, $CsPbCl_3$, in the presence of a trace of iodine as catalyst, was said to react upon heating with ethyl, propyl, and n-butyl iodides and form $RPbI_3$ compounds (225). The mechanism of the reaction was given as follows

$$CsPbCl_3 + RI \longrightarrow RPbCl_3 + CsI$$

$$RPbCl_3 + 3CsI \longrightarrow RPbI_3 + 3CsCl$$

(223) Meyer, Ber., 16, 1439 (1883).
(224) (a) Pfeiffer and Lehnardt, ibid., 36, 1054 (1903).
(b) Pfeiffer, Z. anorg. Chem., 68, 102 (1910).
(225) Lesbre, Compt. rend., 204, 1822 (1937).

5. Methylation of Metallic Salts with Aluminum Carbide.--In all of the literature, there is only one report on the use of a metallic carbide for the preparation of RM compounds. This reaction, however, is important enough to require a separate section for its consideration.

It is well known that aluminum carbide reacts with aqueous acid solutions and evolves methane. Hilpert and Ditmar (226) found that when aluminum carbide was added to an aqueous acid solution of mercuric chloride, methylmercuric chloride was formed in yields as high as 30%. If the acidity of the solution was not too high, dimethylmercury was also produced. A solution of bismuth chloride in 30% hydrochloric acid, when treated with an excess of aluminum carbide, gave a 60% yield of trimethylbismuth. Methyltin trichloride was obtained from the reaction of aluminum carbide with acid solutions of both stannous and stannic chlorides.

6. Metalations with Inorganic Salts.--The displacement of hydrogen from organic molecules, according to the reaction

$$MX + RH \longrightarrow RM + HX$$

is an important means of synthesizing some organometallic compounds. Moissan (227) found that potassium hydride reacted with acetylene and formed potassium acetylide and

(226) Hilpert and Ditmar, Ber., 46, 3738 (1913).
(227) Moissan, Bull. soc. chim., 31, 720 (1904).

hydrogen. A rapid metalation of aromatic hydrocarbons was observed with anhydrous auric chloride (228). If the reaction was stopped before proceeding too far, compounds of the formula, $RAuCl_2$, were formed.

$$RH + AuCl_3 \longrightarrow RAuCl_2 + HCl$$

Mercuration of aromatic compounds by means of inorganic mercury salts takes place easily in many cases. Volhard (229) mercurated thiophene directly, with mercuric chloride. Mercuric acetate was found to react with benzene holologues and give organomercury compounds (230). The direct mercuration of benzene, itself, with mercuric acetate has given 80% yields of phenylmercuric acetate (231). Kharasch and co-workers (232) have further studied the reaction and given a theoretical discussion of the mercuration of aromatic compounds with mercuric acetate. Furan underwent prompt mercuration in the alpha positions and if these were blocked, substitution took place at the beta carbon atoms (233).

A mixture of germanium tetrachloride and dimethylaniline reacted when heated to give a good yield of p-dimethylaminophenylgermanium trichloride, which upon hydrolysis produced

(228) Kharasch and Isbell, J. Am. Chem. Soc., 53, 3053 (1931).
(229) Volhard, Ann., 267, 172 (1892).
(230) Dimroth, Ber., 31, 2154 (1898).
(231) Maynard, J. Am. Chem. Soc., 46, 1510 (1924).
(232) (a) Kharasch and Jacobsohn, Ibid., 43, 1894 (1921).
(b) Kharasch and Chalkley, ibid., 46, 1211 (1924).
(233) Gilman and Wright, ibid., 55, 3302 (1933).

the compound, $[p\text{-}(CH_3)_2NC_6H_4GeO]_2O$ (178).

$$GeCl_4 + p\text{-}(CH_3)_2NC_6H_5 \longrightarrow p\text{-}(CH_3)_2NC_6H_4GeCl_3 + HCl$$

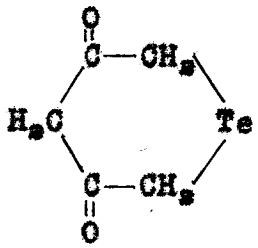
Methylaniline and diethylaniline have also been metalated with germanium tetrachloride (180).

Wieland (234) heated arsenic trichloride and benzene in the presence of aluminum chloride as catalyst. Hydrogen chloride was evolved, and a mixture of triphenylarsenic, diphenylarsenic chloride, and phenylarsenic dichloride was obtained. A reaction between selenium tetrabromide, benzene, and aluminum bromide gave a 25% yield of diphenylselenium (235). By an extension of this reaction, triphenylselenium chloride has been prepared from diphenylselenium dichloride, benzene, and aluminum chloride (236).

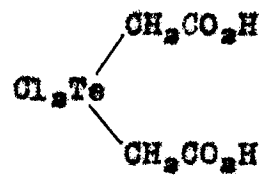
$$(C_6H_5)_2SeCl_2 + C_6H_6 + AlCl_3 \longrightarrow (C_6H_5)_3SeCl + HCl$$

Morgan and co-workers(237) have studied the reactions of tellurium tetrachloride with organic compounds. With acetylacetone, hydrogen chloride was evolved and the cyclic compound [A] was formed (237a). Excess acetic anhydride and tellurium tetrachloride in chloroform yielded compound [B] (237b). Benzene homologues have also been metalated. From dimethylaniline, for example, compound [C] resulted (237c).

(234) Wieland, Ann., 431, 30 (1923).
(235) Leovenich and Sipmann, J. prakt. Chem., 124, 127 (1930).
(236) Leicester and Bergstrom, J. Am. Chem. Soc., 51, 3587 (1929).
(237) (a) Morgan, Cooper and Corby, J. Soc. Chem. Ind., 43, 304 (1924).
(b) Morgan and Drew, J. Chem. Soc., 127, 531 (1925).
(c) Morgan and Burgess, Ibid., 1103 (1929).



[A]



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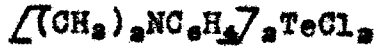


[C]

7. Addition of Inorganic Salts to Carbon-Carbon Double Bonds.--The addition of mercury salts to aliphatic double bonds takes place easily. Hofmann and others (238) have studied these reactions extensively with a great many ethylenic compounds. For example, ethylene, passed into an aqueous suspension of mercuric oxide in the presence of halide ions, reacted in the following manner

$$C_2H_4 + HgO + X^- \longrightarrow HOCH_2CH_2HgX$$

The addition of mercury salts to acetylenes in basic solution leads to di-mercurated derivatives (239), which easily hydrolyze to give carbonyl compounds.

$$RC{\equiv}CR + Hg(X)(OH) \longrightarrow RC(OH)_2C(HgX)_2R \longrightarrow RCH_2COR$$

This reaction is the basis of the industrial production of acetaldehyde from acetylene.

Hall and Nash (240) found that a mixture of ethylaluminum

(238) (a) Hofmann and Sand, Ber., 33, 1340, 1353 (1900); 34, 2907 (1901).
(b) Schoeller, Schrauth and Essers, ibid., 46, 2864 (1913).
(c) Wright, J. Am. Chem. Soc., 57, 1993 (1935).
(239) Nesmejanow and Freidlina, Ber., 69, 1631 (1936).
(240) Hall and Nash, J. Inst. Petroleum Tech., 23, 679 (1937) [C.A., 32, 1239 (1938)].

dichloride and diethylaluminum chloride was formed when a mixture of aluminum and aluminum chloride reacted with ethylene under pressure at 100-200°.

Selenium monochloride apparently underwent direct addition to ethylene (241).

$$2Se_2Cl_2 + 2C_2H_4 \longrightarrow (ClCH_2CH_2)_2SeCl_2 + 3Se$$

8. Preparations from Aryldiazonium Compounds.--The formation of organometallic compounds by the decomposition of aryldiazonium compounds in the presence of metals has been discussed in a previous section. In these reactions, it is believed that free radicals are first formed, and they, in turn, react with the metals. The mechanism by which RM compounds are formed when aryldiazonium compounds decompose in the presence of metallic salts, or when the double salts of metal halides and aryldiazonium compounds are allowed to decompose, has not been satisfactorily explained.

Nesmejanow and co-workers (242) discovered that a very general method and often the best method for preparing aryl RHgX compounds is to allow complex salts of the type, $RN_2Cl \cdot HgCl_2$, to decompose in acetone in the presence of copper powder.

$$RN_2Cl \cdot HgCl_2 + Cu \longrightarrow RHgCl + N_2 + CuCl_2$$

(241) Boord and Cope, J. Am. Chem. Soc., 44, 395 (1922).
(242) (a) Nesmejanow, Ber., 62, 1010 (1929).
(b) Nesmejanow and Kahn, ibid., 62, 1018 (1929).
(c) Nesmejanow, Gluschnew, Epifnasky and Flegontow, ibid., 67, 130 (1934).

By using an excess of copper powder and adding strong ammonia, the RHgCl compound can be reduced to give a good yield of R_2Hg.

When salts of the type $RN_2Cl \cdot SnCl_4$ were decomposed with powdered tin in hot ethyl acetate, yields of from 5 to 20% of R_2SnCl_2 were produced (122). Similarly, $C_6H_5N_2Cl \cdot PbCl_2$, when decomposed with copper powder, gave a very small quantity of diphenyllead oxide. The salt, $C_6H_5N_2Cl \cdot PbCl_4$, produced a small yield of triphenyllead chloride when it was decomposed with zinc in ether (122).

The reaction of an aryldiazonium chloride with sodium arsenite, often called the Bart reaction, is a general method for preparing arylarsonic acids (243). For example, benzenediazonium chloride and sodium arsenite reacted according to the equation

$$C_6H_5N_2Cl + Na_2HAsO_3 \longrightarrow C_6H_5AsO_3HNa + NaCl + N_2$$

Arylstibonic acids have been conveniently synthesized by the reaction of aryldiazonium chlorides on antimony oxide in the presence of alkali and copper powder (244).

$$RN_2Cl + Sb_2O_3 + H_2O \longrightarrow RSbO(OH)_2$$

The preparation of p-fluorophenylstibonic acid by the diazonium method has been broken down into two stages (245). p-Fluorobenzenediazonium chloride and antimony trichloride

(243) Schmidt, Ann., 421, 159 (1920).
(244) Schmidt, Ibid., 421, 174 (1920).
(245) Dyson, Rec. trav. Chim., 57, 1016 (1938).

first formed a yellow complex which upon treatment with dilute sodium hydroxide solution evolved nitrogen and gave the $RSbO(OH)_2$ compound.

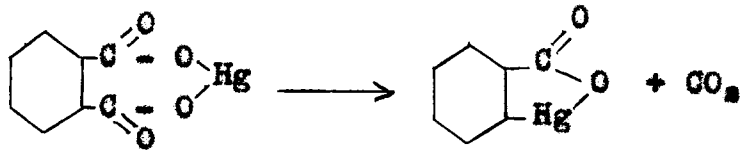
Bismuth chloride forms complex salts with aryldiazonium halides, and these complexes have been utilized for the preparation of organobismuth compounds (246). When $RN_2Cl \cdot BiCl_3$ salts were decomposed with copper powder in the appropriate solvents, $RBiCl_2$ and R_2BiCl derivatives were obtained, usually in rather low yields.

Challenger and Peters (247) have prepared the compound, C_6H_5SeCN, by the reaction of benzenediazonium chloride with aqueous potassium selenocyanate. Through a similar reaction, a 72% yield of diphenylselenium has been obtained (236).

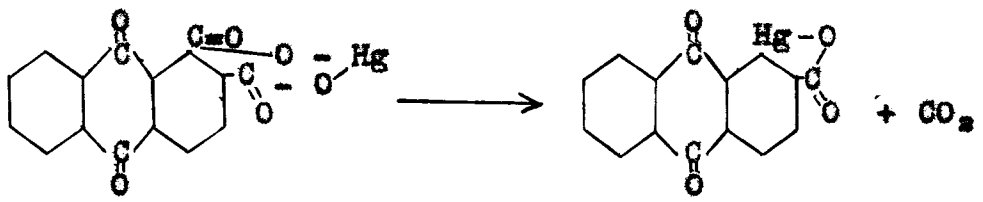
$$2C_6H_5N_2Cl + K_2Se \longrightarrow (C_6H_5)_2Se + 2N_2 + 2KCl$$

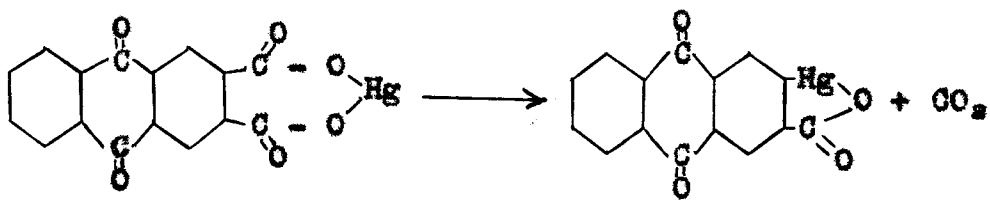
9. The Formation of RM Compounds by the Elimination of Carbon Dioxide from Metal Salts of Organic Acids.--Mercury salts of certain aromatic acids lose carbon dioxide when heated and form organomercury compounds. Pesci (248) first discovered this reaction when he heated sodium phthalate with mercuric acetate in water solution.

(246) (a) Gilman and Svigoon, J. Am. Chem. Soc., 61, 3586 (1939).
(b) Gilman and Yablunky, ibid., 63, 949 (1941).
(247) Challenger and Peters, J. Chem. Soc., 1364 (1928).
(248) Pesci, Atti. accad. Lincei, /5/ 10, 362 (1901) /Chem. Zentr., 72, (2) 108 (1901)/.



Whitmore and Carnahan (249) carried out the two following reactions at temperatures above 200°.





Di-2,4,6,-trinitrophenylmercury and di-2,4-dinitrobenzylmercury were prepared by heating the mercury salts of the corresponding acids (250). Kharasch and Staveley (251) have found that, in general, if an organic acid easily loses carbon dioxide upon heating, its mercury salt will also lose carbon dioxide and yield an organomercury compound.

$$(RCOO)_2Hg \longrightarrow R_2Hg + 2CO_2$$

The organolead salt, $(C_6H_5)_3PbOOCCH_2CO_2C_2H_5$, was said (252) to lose carbon dioxide when heated at 160° under reduced pressure to give the compound, $(C_6H_5)_3PbCH_2COOC_2H_5$.

(249) Whitmore and Carnahan, J. Am. Chem. Soc., 51, 856 (1929).
(250) Kharasch, ibid., 43, 2238 (1921).
(251) Kharasch and Staveley, ibid., 45, 2961 (1923).
(252) Kocheshkov and Aleksandrov, J. Gen. Chem. (U.S.S.R.) 7, 93 (1937) /C.A., 31, 4291 (1937)/.

10. Miscellaneous Methods for Preparing Organomercury Compounds.--The reactions discussed in this section have been applied only to the preparation of organomercury compounds, but possibly only because they have not been tried with other metals.

Hellerman and Newman (253) allowed diazomethane to react with mercuric chloride and obtained a quantitative yield of chloromethylmercuric chloride.

$$CH_2N_2 + HgCl_2 \longrightarrow ClCH_2HgCl + N_2$$

A second molecule of diazomethane reacted to give $(ClCH_2)_2Hg$. Other RHgCl derivatives were converted to the $RHgCH_2Cl$ compounds by diazomethane. Diazodiphenylmethane and mercuric chloride yielded the compound, $(C_6H_5)_2CClHgCl$. A similar reaction between mercuric chloride and diazoacetic ester (254) took place as follows

$$4N_2CHCOOC_2H_5 + 3HgCl_2 \longrightarrow Hg[C(HgCl)ClCOOC_2H_5]_2 + 4N_2 + 2ClCH_2COOC_2H_5$$

The reaction of zinc chloride with diazomethane in ether was believed to yield the compound, $(ClCH_2)_2Zn$, as an unstable intermediate product (255). This, then, reacted with the ether to give the final products represented in the equation.

$$ZnCl_2 + 2CH_2N_2 + (C_2H_5)_2O \longrightarrow ZnO + C_4H_{10}O + C_2H_4Cl_2 + N_2$$

(253) Hellerman and Newman, J. Am. Chem. Soc., 54, 2859 (1932).
(254) Nesmejanow and Powoh, Ber., 67, 971 (1934).
(255) Caronna and Sansone, Atti X°Congr. intern. chim., 3, 77 (1939) [C.A., 34, 980 (1940)].

A general method for preparing aryl-HgCl compounds consists of heating an arylsulfinic acid with an aqueous solution of mercuric chloride (256).

$$RSO_2H + HgCl_2 \longrightarrow RHgCl + SO_2 + HCl$$

Probably a mercury salt, RSO_2HgCl, is first formed and this, when heated, loses SO_2 in much the same way as mercury salts of carboxylic acids lose CO_2.

A reaction between aryl iodoxy compounds and mercuric oxide in water led to the production of organomercury compounds (257). The reaction was most satisfactorily carried out in the presence of silver oxide.

$$RIO_2 + HgO \longrightarrow RHgIO_2$$

By treating the reaction mixtures with an alkali halide such as NaCl, the RHgCl compounds were precipitated and isolated.

III. Interconversion Methods

In this section, methods will be discussed for converting an organometallic compound of a given metal to a different organometallic compound of the same metal. In short, reactions of organometallic compounds will be considered in which the products of the reactions are also organometallic compounds.

1. Metal-Metal Interconversions.--Reactions of the type

$$RM + R'M' \rightleftharpoons R'M + RM'$$

(256) Peters, Ber., 38, 3567 (1905).
(257) Nesmejanow and Makarowa, ibid., 66, 199 (1933).

are, as indicated, reversible processes. There is a striking similarity between these reactions and the classical ionic reactions of inorganic chemistry. In general, the most negative organic radicals will migrate to the most positive metals. Often, however, the course of a reaction is influenced by the insolubility of one of the products in the solvent used.

The exchange between ethyllithium and dimethylmercury in petroleum ether (72) or in benzene (74) solution has been used to prepare methyllithium, which is insoluble and precipitates.

$$2C_2H_5Li + (CH_3)_2Hg \longrightarrow (C_2H_5)_2Hg + 2CH_3Li$$

In the same way, phenyllithium was obtained from ethyllithium and diphenylmercury (73, 74). Pure samples of benzyllithium have been prepared from dibenzylmercury and ethyllithium in benzene solution (74), and from dibenzylmercury and n-butyllithium in ether solution (258). The reversibility of the reaction

$$(C_6H_5)_2Hg + 2p\text{-}CH_3C_6H_4Li \rightleftharpoons (p\text{-}CH_3C_6H_4)_2Hg + 2C_6H_5Li$$

has been demonstrated (259).

A reaction between phenyllithium and benzylmagnesium chloride gave benzyllithium as one product (73).

$$C_6H_5CH_2MgCl + 2C_6H_5Li \longrightarrow C_6H_5CH_2Li + (C_6H_5)_2Mg + LiCl$$

By a similar reaction, isopropyllithium was prepared starting with phenyllithium and isopropylmagnesium chloride (73).

(258) Ziegler and Schäfer, Ann., 479, 150 (1930).
(259) Gilman and Jones, J. Am. Chem. Soc., 63, 1439 (1941).

These reactions between Grignard reagents and lithium compounds are probably reversible, because the aliphatic derivative, n-butyllithium, in a reaction with diphenylmagnesium, has been converted to phenyllithium (259).

$$2RLi + R'_2Mg \rightleftharpoons 2R'Li + R_2Mg$$

n-Butyllithium underwent a prompt interconversion with triphenylthallium in ether solution to give phenyllithium and tri-n-butylthallium (166). Aromatic R_3Pb and R_4Pb compounds (260) have been shown to undergo interchange reactions with n-butyllithium to form aromatic RLi derivatives and n-butyllead compounds. Aromatic R_4Sn compounds underwent interconversion reactions with n-butyllithium equally as readily as did the corresponding R_4Pb compounds (261). Triarylbismuth compounds (262) and similar derivatives of antimony (263) gave products resulting from metal-metal interchanges with n-butyllithium.

$$R_3Bi + 3n\text{-}C_4H_9Li \longrightarrow 3RLi + (n\text{-}C_4H_9)_3Bi$$

A reaction between n-butyllithium and diphenylselenium gave phenyllithium and phenyl-n-butylselenium (264). Ether solutions of n-butyllithium did not react with triphenylarsenic or tetraphenylgermanium under the ordinary conditions (263).

(260) Gilman and Moore, ibid., 62, 3206 (1940).
(261) Moore, Doctoral Dissertation, Iowa State College (1941).
(262) Gilman, Yablunky and Svigoon, J. Am. Chem. Soc., 61, 1170 (1939).
(263) Unpublished study by L. Woods.
(264) Gilman and Bebb, J. Am. Chem. Soc., 61, 109 (1939).

n-Butylsodium, like the lithium analogue, has shown a number of metal-metal interconversion reactions. A petroleum ether suspension of n-butylsodium with diphenylmercury gave phenylsodium and di-n-butylmercury (264). Similar reactions of n-butylsodium with aryl R_3Bi compounds yielded arylsodium derivatives and tri-n-butylbismuth (262).

The interconversion of organomagnesium and organomercury compounds was probably first observed by Challenger and Ridgway (196). These authors found that a reaction between phenylmercuric bromide and α-naphthylmagnesium bromide gave di-α-naphthylmercury and phenylmagnesium bromide.

$$C_6H_5HgBr + 2C_{10}H_7MgBr \longrightarrow (C_{10}H_7)_2Hg + C_6H_5MgBr + MgBr_2$$

Kharasch and Swartz (265) obtained diphenylmercury from phenylmagnesium bromide and allylmercuric iodide.

$$CH_2{=}CHCH_2HgI + 2C_6H_5MgBr \longrightarrow (C_6H_5)_2Hg + CH_2{=}CHCH_2MgBr + MgBrI$$

As a matter of fact, mercury-magnesium interconversions take place quite readily in ether solution, and proof has been presented for the reversibility of the reaction between phenylmagnesium bromide and di-p-tolylmercury (259).

$$2C_6H_5MgBr + (p\text{-}CH_3C_6H_4)_2Hg \rightleftharpoons 2p\text{-}CH_3C_6H_4MgBr + (C_6H_5)_2Hg$$

A concentrated solution of diphenylmercury in diethylzinc, on standing, was apparently partially transformed into diphenylzinc and diethylmercury (74). Diphenylmercury and tri-α-naphthylbismuth were heated to 200° and among the

(265) Kharasch and Swartz, J. Org. Chem., 3, 405 (1938).

products were isolated di-α-naphthylmercury, and triphenylbismuth, and diphenyl-α-naphthylbismuth (196). Diphenylmercury and tri-p-tolylbismuth underwent a similar interconversion.

Extensive studies have been reported by Calingaert and co-workers (266) on reactions between two or more different organometallic compounds of the same metal. The products of such reactions are mixtures resulting from a random distribution of the organic radicals. Most of the studies have been concerned with organolead compounds (266a, b), but R_2Hg, R_4Sn, and R_4Si systems have also been shown to undergo redistribution reactions (266d). Unless the system under examination contains an organometallic halide (266c), the presence of a catalyst such as aluminum chloride is usually necessary before a redistribution reaction will take place. Mixtures consisting of two different organometallic compounds also undergo exchange reactions to give all of the possible products (266e, f).

(266) (a) Calingaert and Beatty, J. Am. Chem. Soc., 61, 2748 (1939); Calingaert, Beatty and Neal, ibid., 61, 2755 (1939); Calingaert and Soroos, ibid., 61, 2758 (1939); Calingaert, Beatty and Hess, ibid., 61, 3300 (1939).
(b) Calingaert, Beatty and Soroos, ibid., 62, 1099 (1940).
(c) Calingaert, Soroos and Shapiro, ibid., 62, 1104 (1940).
(d) Calingaert, Soroos and Hnizda, ibid., 62, 1107 (1940).
(e) Calingaert, Soroos and Thomson, ibid., 62, 1542 (1940).
(f) Calingaert, Soroos and Shapiro, ibid., 63, 947 (1941).

2. Hydrogen-Metal Interconversions.--Hydrogen-metal interconversions or metalation reactions are characteristic of the more highly reactive organometallic compounds. These reactions, represented in the equation

$$RM + R'H \longrightarrow R'M + RH$$

are of prime importance in the synthesis of many organometallic derivatives of lithium, sodium, and potassium.

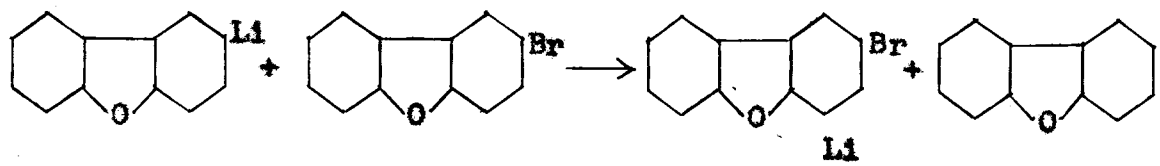
Ether solutions of n-butyllithium have been used extensively as metalating agents. In general, the substitution of lithium for hydrogen takes place at a carbon atom ortho to a sulfur, nitrogen, or an oxygen linkage if these atoms are present in the aromatic molecule. N-Ethylcarbazole was allowed to react with n-butyllithium, and subsequent to carbonation, a 23% yield of N-ethylcarbazole-4-carboxylic acid was obtained (267). Metalation of such molecules as methoxydibenzofurans, diphenyl ether, anisole, diphenylsulfide (264), phenols and methoxybenzenes (268), dibenzothiophene (269), and others, using n-butyllithium, has generally given good yields of the ortho lithio derivatives. An interesting case in which lithium did not enter the position ortho to a sulfur linkage was the metalation of methyl phenyl sulfide using n-butyllithium. The chief product from this reaction was the compound, $C_6H_5SCH_2Li$, obtained in a 62% yield

(267) Gilman and Kirby, J. Org. Chem., 1, 146 (1936).
(268) Gilman, Willis, Cook, Webb and Meals, J. Am. Chem. Soc., 62, 667 (1940).
(269) Gilman and Jacoby, J. Org. Chem., 3, 108 (1938).

(270). In the reaction of n-butyllithium with triphenylamine, the lithium atom entered a meta position (271). The other product from each of these metalation reactions using n-butyllithium is, of course, n-butane.

$$n\text{-}C_4H_9Li + RH \longrightarrow RLi + n\text{-}C_4H_{10}$$

Organolithium compounds other than n-butyllithium are also effective metalating agents. Reactions of phenyllithium and α-naphthyllithium with dibenzothiophene have given 4-lithiodibenzothiophene (269). p-Anisyllithium reacted with p-anisyl bromide and formed 3-methoxy-5-bromophenyllithium (272). A similar reaction was that of 3-lithiodibenzofuran with 3-bromodibenzofuran (272).



Organosodium compounds are more reactive metalating agents than the corresponding RLi compounds. Schorigin (273) found that phenylsodium was readily formed by the reaction between an alkylsodium compound and benzene.

$$RNa + C_6H_6 \longrightarrow C_6H_5Na + RH$$

When phenylsodium was heated in toluene a lateral hydrogen atom in toluene was displaced and benzylsodium formed (6,

(270) Gilman and Webb, J. Am. Chem. Soc., 62, 987 (1940).
(271) Gilman and Brown, ibid., 62, 3208 (1940).
(272) Gilman, Langham and Willis, ibid., 63, 346 (1940).
(273) Schorigin, Ber., 41, 2717 (1908).

274). Also, phenylsodium and n-butylsodium metalated β-methylnaphthalene laterally (6). Both phenylsodium and n-butylsodium have been used to metalate anisole and yield o-methoxyphenylsodium (264). Phenylacetylene reacted with ethynylsodium to give phenylethynylsodium (264). Conant and Wheland (275) carried out exchange reactions between hydrocarbons and both RNa and RK compounds in order to determine the relative acidities of the selected hydrocarbons.

$$RNa + R'H \rightleftharpoons R'Na + RH$$

Organopotassium compounds are highly active metalating agents. One of the best and easiest methods of preparing phenylpotassium is the reaction of an alkyl RK compound with benzene (137, 276). Although phenylsodium can be prepared from sodium and chlorobenzene in toluene, the reaction of potassium with chlorobenzene in toluene, even at low temperatures, gave a high yield of benzylpotassium (6).

$$2K + C_6H_5Cl \longrightarrow C_6H_5K + KCl$$

$$C_6H_5K + C_6H_5CH_3 \longrightarrow C_6H_5CH_2K + C_6H_6$$

Reactions between the free metals and di-n-butylmercury in benzene solution have been used to prepare phenylrubidium and phenylcesium as well as phenylpotassium (277)

$$2M + (n\text{-}C_4H_9)_2Hg \longrightarrow 2n\text{-}C_4H_9M$$

$$n\text{-}C_4H_9M + C_6H_6 \longrightarrow C_6H_5M + n\text{-}C_4H_{10}$$

(274) Morton and Fallwell, J. Am. Chem. Soc., 60, 1429 (1938).
(275) Conant and Wheland, ibid., 54, 1212 (1932).
(276) Gilman and Kirby, ibid., 58, 2074 (1936).
(277) Gilman, Jacoby and Ludeman, ibid., 60, 2336 (1938).

Compared with the organoalkali compound, Grignard reagents are very weak metalating agents. Alkyllithium compounds react immediately with triphenylmethane and give triphenylmethyllithium, while triphenylmethane is unchanged by Grignard reagents under the same conditions (139). Challenger and Miller (278) heated ethylmagnesium bromide with phenetole, anisole, and dimethylaniline to about 200° for periods of several hours. In each case, metalation occurred at the position ortho to the oxygen or nitrogen linkage. Thus, ethylmagnesium bromide with anisole gave ethane and o-anisylmagnesium bromide. Ethylmagnesium bromide reacted with acetylene to give ethynylmagnesium bromide (279).

Phenylcalcium iodide metalated dibenzofuran at the 4-position (17). The related reaction of phenylcalcium iodide with dibenzothiophene, however, yielded dibenzothiophene-3-calcium iodide (269, 280).

3. Halogen-Metal Interconversions.--The recently discovered halogen-metal interconversion reactions have been most extensively studied using organolithium compounds. From n-butyllithium and aromatic bromides or iodides, a large number of aromatic lithium derivatives have been prepared. The reactions are best conducted in ether solution.

$$n\text{-}C_4H_9Li + RBr \longrightarrow RLi + n\text{-}C_4H_9Br$$

(278) Challenger and Miller, J. Chem. Soc., 894 (1938).
(279) Kleinfeller and Lohmann, Ber., 71, 2608 (1938).
(280) Gilman, Jacoby and Pacevitz, J. Org. Chem., 3, 120 (1938).

Among the halogen compounds which have been converted to the lithium derivatives by means of the above reaction are o-bromoanisole (281a), bromodibenzofurans (281b), m- and p-bromodimethylaniline (281c), and a large series of aromatic bromides and iodides (281d). Gilman and Moore (282) have studied the interconversions of a number of RLi compounds with α-bromonaphthalene, and they have noted the effects of solvents, time, temperature, and catalysts on the reactions. Different methoxybromodibenzofurans with n-butyllithium gave, in all cases, halogen-metal interconversions rather than hydrogen-metal exchanges (283). The results of low-temperature reactions of n-butyllithium with 3-bromopyridine and 3-bromoquinoline were halogen-lithium exchanges rather than addition to the anil linkages (284). Subsequent to carbonation, good yields of nicotinic acid and quinoline-3-carboxylic acid were obtained.

Langham, Brewster, and Gilman (285) studied the reactions of phenyl-, methyl-, and n-butyllithium with a series of halogenated phenyl ethers. Halogen-metal interconversions occurred with the bromo and iodo compounds but not with the

(281) (a) Gilman, Langham and Jacoby, J. Am. Chem. Soc., 61, 106 (1939).
(b) Gilman, Willis and Swislowsky, ibid., 61, 1371 (1939).
(c) Gilman and Banner, ibid., 62, 344 (1940).
(d) Gilman, Langham and Moore, ibid., 62, 2327 (1940).
(282) Gilman and Moore, ibid., 62, 1843 (1940).
(283) Gilman, Swislowsky and Brown, ibid., 62, 348 (1940).
(284) Gilman and Spatz, ibid., 62, 446 (1940).
(285) Langham, Brewster and Gilman, ibid., 63, 545 (1941).

chloro compounds. Only two examples of chlorine-lithium exchanges are known at present (281d). Phenylethynyl chloride reacted with n-butyllithium at 0° to give, after thirty minutes, a 15% yield of phenylethynyllithium. A chlorine-lithium exchange took place also between n-butyllithium and 2,4,5-triphenyl-3-chlorofuran. No fluorine-lithium interconversions have been reported.

The halogen-lithium exchanges are generally rapid and are reversible reactions. All four possible products were obtained from the reactions of either phenyllithium with p-iodotoluene or p-tolyllithium with iodobenzene (286).

$$C_6H_5Li + p\text{-}CH_3C_6H_4I \rightleftharpoons p\text{-}CH_3C_6H_4Li + C_6H_5I$$

Aliphatic iodides were found to undergo iodine-lithium exchange reactions with aliphatic lithium compounds at low temperatures (286). Here, again, the reaction was reversible.

$$C_6H_5Li + n\text{-}C_4H_9I \rightleftharpoons C_6H_5I + n\text{-}C_4H_9Li$$

One example of a halogen-metal interconversion with an organosodium compound has been reported (286).

Ordinarily, neither Grignard reagents nor any other organometallic compounds than those of the alkali metals appear to undergo halogen-metal interconversion reactions. However, in the presence of a trace of RLi compound, halogen-mercury interconversions readily took place between aryl iodides and organomercury compounds (287). The catalytic effect of the

(286) Gilman and Jones, ibid., 63, 1441 (1941).
(287) Gilman and Jones, ibid., 63, 1443 (1941).

RLi compound can be explained by the following series of reactions

$$R_2Hg + 2R'Li \rightleftharpoons 2RLi + R'_2Hg \quad \text{.....[A]}$$

$$2RLi + 2R'I \rightleftharpoons 2R'Li + 2RI \quad \text{.....[B]}$$

$$R_2Hg + 2R'I \rightleftharpoons R'_2Hg + 2RI \quad \text{.....[C]}$$

Addition of equations [A] and [B] gives equation [C]. As indicated, reaction [C] is reversible. Similar interconversion reactions did not take place between aryl iodides and tetraethyllead. Probably, the more reactive organometallic compounds of the second and third group metals will undergo catalyzed halogen-metal exchanges.

Marquardt (201b) heated tri-i-butylbismuth with methyl iodide to 150° in a sealed tube and reported that trimethylbismuth was formed. In a similar manner, tri-i-butylbismuth and ethyl iodide supposedly gave triethylbismuth. The trimethyl- and triethylbismuth were identified only by odor.

4. Reactions of RMM' Compounds in Liquid Ammonia.--The fourth group elements, silicon, germanium, tin, and lead form compounds of the type R_3MNa, which can react with various halogen compounds and yield R_3MR' derivatives.

$$R_3MNa + R'X \longrightarrow R_3MR' + NaX$$

Liquid ammonia is the solvent generally used for these reactions.

Kraus and co-workers (176, 288) prepared $(C_6H_5)_3GeNa$

(288) (a) Kraus and Nutting, ibid., 54, 1622 (1932).
(b) Kraus and Sherman, ibid., 55, 4694 (1933).

by the reaction of sodium in liquid ammonia with the compound, $(C_6H_5)_3Ge-Ge(C_6H_5)_3$. Triphenylgermanium-sodium reacted readily with alkyl halides. For instance, $(C_6H_5)_3GeNa$ with methyl iodide, ethyl bromide (288a), or other alkyl bromides (288b), formed the unsymmetrical $(C_6H_5)_3GeR$ derivatives. The reaction of triphenylgermanium-sodium with trimethyltin bromide gave the compound, $(C_6H_5)_3Ge-Sn(CH_3)_3$ (176). A similar reaction with triethylgermanium bromide, carried out in benzene, yielded the derivative, $(C_6H_5)_3Ge-Ge(C_2H_5)_3$ (288b).

$$(C_6H_5)_3GeNa + (C_2H_5)_3GeBr \longrightarrow (C_6H_5)_3Ge-Ge(C_2H_5)_3 + NaBr$$

The $R_3Si-SiR_3$ compounds apparently do not react with sodium or the other alkali metals to form R_3SiM compounds. Only one R_3SiM compound, triethylsilicon-lithium, has been reported (289); and this was prepared according to the following reactions

$$(C_6H_5)_3GeNa + (C_2H_5)_3SiBr \longrightarrow (C_6H_5)_3Ge-Si(C_2H_5)_3 + NaBr$$

$$(C_6H_5)_3Ge-Si(C_2H_5)_3 + 2Li \longrightarrow (C_6H_5)_3GeLi + (C_2H_5)_3SiLi$$

The second reaction was carried out in ethylamine solution. Ethyl bromide reacted with triethylsilicon-lithium and gave tetraethylsilicon.

Trimethyltin halides reacted with one equivalent of sodium in liquid ammonia and quantitatively formed trimethyltin (290). A second equivalent of sodium converted

(289) Kraus and Nelson, ibid., 56, 195 (1934).
(290) Kraus and Sessions, ibid., 47, 2361 (1925).

trimethyltin to trimethyltin-sodium.

$$(CH_3)_3SnX + Na \longrightarrow (CH_3)_3Sn + NaX$$

$$(CH_3)_3Sn + Na \longrightarrow (CH_3)_3SnNa$$

By the same reaction, triphenyltin-sodium has been prepared from triphenyltin halides and sodium (291). Triphenyltin-sodium, like the corresponding germanium compound, reacted readily with organic halides and yielded $(C_6H_5)_3SnR$ compounds (291). Diphenyltin dichloride reacted with sodium in liquid ammonia and the product was diphenyltin-disodium, $(C_6H_5)_2SnNa_2$. This compound was transformed into an organotin hydride by ammonium bromide (291).

$$(C_6H_5)_2SnNa_2 + 2NH_4Br \longrightarrow (C_6H_5)_2SnH_2 + 2NaBr + 2NH_3$$

Gilman and Baillie (191d) prepared a series of R_3PbNa compounds by the reaction

$$R_3PbX + 2Na \longrightarrow R_3PbNa + NaX$$

Reactions with ethyl and benzyl halides gave the unsymmetrical R_3PbR' derivatives.

$$R_3PbNa + R'X \longrightarrow R_3PbR' + NaX$$

Recently, a number of R_2BiM compounds have been prepared in liquid ammonia from aryl R_2BiX derivatives and alkali and alkaline earth metals (292).

$$R_2BiX + 2M \longrightarrow R_2BiM + MX$$

The diarylbismuth-sodium compounds reacted, in liquid ammonia, with aryl bromides or iodides and were converted to R_2BiR'

(291) Chambers and Scherer, ibid., 48, 1054 (1926).
(292) Gilman and Yablunky, ibid., 63, 212 (1941).

types. These reactions have been recommended for the synthesis of unsymmetrical organobismuth compounds (292).

5. Disproportionation of RMX Compounds to Give the R_2M Types.--Under the proper treatment, certain mixed organometallic compounds, RMX, can be converted to the symmetrical derivatives without the aid of reducing agents.

$$2RMX \longrightarrow R_2M + MX_2$$

Heating organoberyllium halides caused their disproportionation into R_2Be and BeX_2 (8), and the R_2Be product could, in some cases, be distilled from the mixture.

Gilman and Brown (293) heated methylmagnesium chloride in a high vacuum and were able to distil some dimethylmagnesium from the mixture. A much better method of bringing about the disproportionation of Grignard reagents, however, is to precipitate the halides from the ether solution by means of dioxane (294). The R_2Mg compound, which is normally present due to the equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$

remains in solution while the RMgX and MgX_2 are precipitated as insoluble dioxane complexes. When the precipitates are shaken for several hours with the ether solutions, the latter become richer in R_2Mg compound (294c).

In his pioneer work on the reactions of alkyl halides

(293) Gilman and Brown, ibid., 52, 5045 (1930).
(294) (a) Schlenk and Schlenk, Ber., 62, 920 (1929).
(b) Cope, J. Am. Chem. Soc., 57, 3238 (1935).
(c) Noller and White, ibid., 59, 1354 (1937).

with zinc, Frankland (30) found that the R_2Zn compounds could be distilled from the reaction mixtures leaving the zinc halide behind.

$$2RZnX \longrightarrow R_2Zn + ZnX_2$$

Several methods have been devised for converting arylmercuric compounds to diarylmercury derivatives by tying up part of the mercury in the form of complex salts (295). Heating arylmercuric iodides with sodium iodide in alcohol has given almost quantitative yields of the R_2Hg compound (295a).

$$2RHgI + 2NaI \longrightarrow R_2Hg + Na_2HgI_4$$

Buckton (295b) heated organomercuric cyanides with potassium cyanide and the following reaction took place

$$2RHgCN + 2KCN \longrightarrow R_2Hg + K_2Hg(CN)_4$$

A reaction similar to the above two is that of organomercuric thiosulfates with sodium thiosulfate (295c).

$$(RHg)_2S_2O_3 + Na_2S_2O_3 \longrightarrow R_2Hg + Na_2Hg(S_2O_3)_2$$

Dreher and Otto (296) prepared R_2Hg compounds by heating $(RHg)_2S$ compounds.

$$(RHg)_2S \longrightarrow R_2Hg + HgS$$

The distillation of methylaluminum diiodide caused an almost complete disproportionation to dimethylaluminum iodide and aluminum iodide (36b).

(295) (a) Whitmore and Sobatzki, J. Am. Chem. Soc., 55, 1128 (1933).
(b) Buckton, Ann., 108, 103 (1858).
(c) Pesci, Z. anorg. Chem., 15, 208 (1897).
(296) Dreher and Otto, Ber., 2, 542 (1869).

A convenient synthesis of certain triarylantimony compounds consists of heating arylantimony oxides in an atmosphere of carbon dioxide (297).

$$3RSbO \longrightarrow R_3Sb + Sb_2O_3$$

The reverse of the processes described in this section, namely, the reaction of a metallic halide with a symmetrical RM compound of the same metal, appears to be an entirely general reaction.

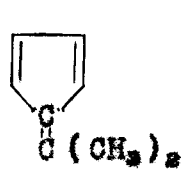
$$R_2M + MX_2 \longrightarrow 2RMX$$

6. The Addition of Organoalkali Compounds to Carbon-Carbon Double Bonds.--A reaction characteristic of the highly reactive organoalkali compounds is addition to carbon-carbon double bonds.

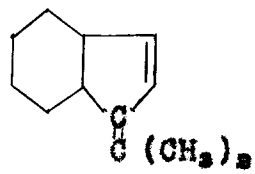
$$RCH{=}CHR + R'M \longrightarrow RCH(R')CH(M)R$$

n-Butyllithium added to the double bond in unsymmetrical diphenylethylene and gave the compound, $(C_6H_5)_2CLiCH_2(n\text{-}C_4H_9)$ (298). A similar addition reaction took place between stilbene and n-butyllithium. Although phenyllithium apparently reacted slowly with unsymmetrical diphenylethylene, benzyllithium and isopropyllithium were reported (73) to add rapidly to the double bond of diphenylethylene and give the $(C_6H_5)_2CLiCH_2R$ compounds. Ziegler and Schäfer (299) studied the addition of phenyllithium to the four fulvene compounds

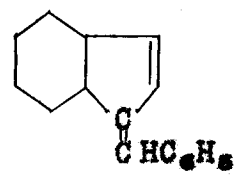
(297) Schmidt, Ann., 421, 233 (1920); ibid., 429, 123 (1922).
(298) Ziegler, Crossmann, Kleiner and Schäfer, ibid., 473, 1 (1929)
(299) Ziegler and Schäfer, ibid., 511, 101 (1934).



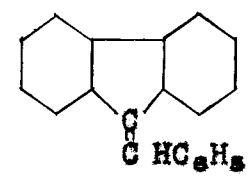
[A]



[B]

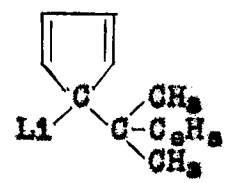


[C]



[D]

From compound [A] the product was the new organolithium compound, [E].



[E]

Compounds [B], [C], and [D] gave analogous products.

Phenylisopropylpotassium has shown addition to carbon-carbon double bonds in a large number of hydrocarbon compounds (300).

The addition of organoalkali compounds to carbon-carbon double bonds has been postulated as the mechanism by which certain unsaturated hydrocarbons are polymerized to high molecular weight substances by alkali metals (301).

7. Addition of Organic Halides to Lower Valent RM Compounds.--A few of the metals form several series of organometallic compounds in which the metals are in different states of valence. With tin, for example, compounds of the

(300) (a) Ziegler and Bähr, Ber., 61, 253 (1928).
(b) Ziegler and Kleiner, Ann., 473, 57 (1929).
(301) Bergmann and co-workers, Ann., 480, 49, 59 (1930).

types R_2Sn, R_3Sn, and R_4Sn are well known. Often, the lower valent compounds will add organic halides and form the higher valent derivatives.

An organogermanium compound represented as $(C_2H_5GeI)_x$ was reported to react with ethyl iodide and yield $(C_2H_5)_2GeI_2$ (302). This is the most satisfactory method for preparing the latter compound.

Pfeiffer (188a) heated diethyltin with ethyl iodide in a sealed tube and prepared triethyltin iodide.

$$(C_2H_5)_2Sn + C_2H_5I \longrightarrow (C_2H_5)_3SnI$$

According to Grüttner (303), methyl iodide reacted with triethyltin at 180° and formed methyltriethyltin and triethyltin iodide.

$$2(C_2H_5)_3Sn + CH_3I \longrightarrow (C_2H_5)_3SnCH_3 + (C_2H_5)_3SnI$$

The reactions of other alkyl iodides with R_3Sn compounds, however, did not give the same results. The products from the reaction of ethyl iodide with triethyltin at 220° were triethyltin iodide and butane (304). Dicyclohexyltin reacted with cyclohexyl bromide as follows (305)

$$(C_6H_{11})_2Sn + 2C_6H_{11}Br \longrightarrow (C_6H_{11})_2SnBr_2 + (C_6H_{11})_2$$

According to the following reactions, free mercury and unsymmetrical tin compounds were formed (306).

(302) Horvitz and Flood, J. Am. Chem. Soc., 55, 5055 (1933).
(303) Grüttner, Ber., 50, 1808 (1917).
(304) Ladenburg, ibid., 4, 19 (1871).
(305) Krause and Pohland, ibid., 57, 532 (1924).
(306) Nesmejanov, Kocheshkov and Fuzyreva, J. Gen. Chem. (U.S.S.R.), 7, 118 (1937) /C.A., 31, 4290 (1937)/.

$$(C_2H_5)_2Sn + (C_6H_5)_2Hg \longrightarrow (C_2H_5)_2Sn(C_6H_5)_2 + Hg$$

$$2(C_2H_5)_2Sn + R_2Hg \longrightarrow 2(C_2H_5)_2SnR + Hg$$

These reactions, although not strictly related to the others in this section, are included here because they are the only examples of their kind.

Michaelis and his students (307) prepared many arsenic compounds of the types $R_3R'AsI$ and $R_3R'_2AsI$ by heating organic iodides with R_3As and $R_2R'As$ compounds.

$$R_3As + R'I \longrightarrow R_3R'AsI$$

The R_3Sb compounds also add alkyl iodides and form pentavalent organoantimony types, R_4SbI (197b, 308).

Pieverling (309) found that diethylselenium added ethyl iodide to give triethylselenium iodide. Similarly, diaryltellurides add alkyl iodides, and by this reaction, quantitative yields of such compounds as methyldi-*p*-anisyltellurium iodide and diphenylbenzyltellurium iodide have been prepared (310).

8. Reduction of RMX Compounds.--The reduction of an organometallic compound represented by the formula RMX, may give the symmetrical R_2M compound, a dimerized product, RM-MR, or an organometallic compound, RM, with the metal in a lower state of valence.

(307) LaCoste and Michaelis, Ber., 11, 1883 (1878); Michaelis and Paetow, Ann., 233, 60 (1886); Michaelis, ibid., 321, 141 (1902).
(308) Loewig, Ann., 97, 322 (1856).
(309) Pieverling, Ber., 9, 1469 (1876).
(310) Lederer, ibid., 48, 1345 (1915); 50, 238 (1917).

Kraus (311) electrolyzed liquid ammonia solutions of methyl-, ethyl-, propyl-, and amylmercuric chlorides and obtained the metal-like (RHg) compounds. The methyl and ethyl derivatives were the most stable, but even they decomposed rapidly at room temperature to give mercury and the R_2Hg compounds. The electrolysis of a 25% water solution of methylmercuric acetate at 30 to 40° gave a 90% yield of dimethylmercury (312). Almost quantitative yields of R_2Hg compounds were obtained by electrolyzing $(RHg)_2SO_4$ solutions (313). R_2Hg compounds have been obtained from the organomercuric halides by reduction with sodium (296), sodium stannite (314a), copper powder in pyridine (314b), or hydrazine (314c).

$$2RHgX \longrightarrow R_2Hg + Hg$$

The reduction of organoaluminum halides, $RAlX_2$, R_2AlX or mixtures of the two, with either sodium or sodium-potassium alloy has given good yields of R_3Al compounds (36b). By carefully controlling the quantity of sodium used, the $RAlX_2$ compounds have been reduced to R_2AlX types.

$$2RAlX_2 + 2Na \longrightarrow R_2AlX + Al + 3NaX$$

Dimethylgallium has been obtained from the reaction of sodium on dimethyl gallium chloride (315).

(311) Kraus, J. Am. Chem. Soc., 35, 1732 (1913).
(312) Maynard and Howard, J. Chem. Soc., 123, 960 (1923).
(313) Melnikov and Rokitskaya, J. Gen. Chem. (U.S.S.R.), 7, 2596 (1937) /C.A., 32, 2084 (1938)/.
(314) (a) Dimroth, Ber., 35, 2853 (1902).
(b) Hein and Wagler, ibid., 58, 1499 (1925).
(c) Gilman and Barnett, Rec. trav. chim., 55, 563 (1936).
(315) Kraus and Toonder, J. Am. Chem. Soc., 55, 3547 (1933).

$$(CH_3)_2GaCl + Na \longrightarrow (CH_3)_2Ga + NaCl$$

Diphenylthallium bromide reacted with sodium in liquid ammonia and gave triphenylthallium as one product (166).

$$3(C_6H_5)_2TlBr + 3Na \longrightarrow 2(C_6H_5)_3Tl + 2Tl + 2NaBr$$

Germanium compounds of the type $R_3Ge-GeR_3$ have been synthesized by heating the R_3GeBr compounds with sodium in xylene (179) or in the absence of a solvent (316). The reduction of diphenylgermanium dichloride with sodium in xylene gave 10 to 20% yields of diphenylgermanium (317).

$$(C_6H_5)_2GeCl_2 + 2Na \longrightarrow (C_6H_5)_2Ge + 2NaCl$$

Ethylgermanium triiodide was reduced by heating with excess 40 to 60% lead-bismuth alloy (302). The product was thought to have the formula, $(C_2H_5GeI)_x$.

The reduction of diethyltin dichloride with 20% sodium amalgam gave diethyltin according to Pfeiffer (188a). The same compound was obtained much earlier by Loewig (318) from the reaction of ethyl iodide with a sodium-rich tin alloy. Frankland (39) also prepared diethyltin by the reduction of diethyltin dichloride with zinc.

$$(C_2H_5)_2SnCl_2 + Zn \longrightarrow (C_2H_5)_2Sn + ZnCl_2$$

Phenyltin trichloride was reduced with sodium, and the products were tetraphenyltin, tin, and sodium chloride (319).

The electrolysis of triethyllead hydroxide in 95%

(316) Kraus and Flood, ibid., 54, 1635 (1932).
(317) Kraus and Brown, ibid., 52, 4031 (1930).
(318) Loewig, Ann., 84, 319 (1852).
(319) Schwarz and Reinhardt, Ber., 65, 1743 (1932).

alcohol solution gave triethyllead (320). Lead electrodes were used, and the triethyllead formed as a heavy oil at the cathode.

Gilman and Yablunky (321) have used hydrazine to reduce the arylbismuth halides, $RBiX_2$ and R_2BiX, to give the R_3Bi compounds in excellent yields. Sodium in liquid ammonia reacted with diphenylbismuth bromide to give, first, diphenylbismuth-sodium (293). The diphenylbismuth-sodium then slowly decomposed and formed triphenylbismuth in a 49% yield.

Hein (322) found that pentaphenylchromium hydroxide spontaneously lost a phenyl group when it reacted with mineral acids or alkali halides.

$$(C_6H_5)_5CrOH + HI \qquad (C_6H_5)_4CrI + C_6H_5. + H_2O$$

When tetraphenylchromium iodide was electrolyzed in liquid ammonia, tetraphenylchromium was formed as an insoluble, red, metal-like precipitate (323). Likewise, the reduction of triphenylchromium iodide in liquid ammonia, either electrolytically or with sodium, gave triphenylchromium as a yellow brown precipitate (324).

$$(C_6H_5)_3CrI + Na \qquad (C_6H_5)_3Cr + NaI$$

Table I contains a resume of all of the methods of preparing organometallic compounds, together with the pages on which these methods are discussed.

(320) Midgley, Hochwalt and Calingaert, J. Am. Chem. Soc., 45, 1821 (1923).
(321) Gilman and Yablunky, ibid., 62, 665 (1940).
(322) Hein, Ber., 54, 2708 (1921).
(323) Hein and Eissner, ibid., 59, 362 (1926).
(324) Hein and Markert, ibid., 61, 2255 (1928).

Table I

Index of General Methods for Preparing Organometallic Compounds

Table I (continued)

Table I (continued)

Table I (continued)

* This type of reaction has sometimes been designated as a metalation reaction. Here it is referred to as hydrogen-metal interconversion to distinguish it from the other two types of metalation reactions, displacement of hydrogen by a metal (I,6c) and substitution of hydrogen by a metal of a metallic halide (III,4a).

Table I (continued)

** Redistribution is defined as a reaction in which the equilibrium is governed by the laws of random distribution, ref. (266). Here it refers to reactions between RM compounds containing different metals.

Organometallic Compounds of Titanium, Zirconium, and Lanthanum

During the past eighty years no less than eight different workers have investigated the problem of preparing organotitanium compounds, and many studies have probably been made and not reported. No one, however, has yet succeeded in preparing a compound containing a carbon-titanium bond.

The first reported attempt at the preparation of organotitanium compounds was that of Cahours (58) who obtained only a black reaction product of unknown composition from titanium tetrachloride and diethylzinc. Powdered titanium metal did not react with methyl iodide or ethyl iodide at 210-220°.

Köhler (325) observed that when phenylphosphorus dichloride and titanium tetrachloride were mixed, heat was evolved with the formation of a dark red-violet liquid. Distillation of the liquid, however, yielded the two original components unchanged.

Schumann (326) found that the reaction of titanium tetrachloride with diethylzinc under a variety of conditions always led to the production of large quantities of gas and the formation of reduction products of titanium tetrachloride. No ethyltitanium compounds were obtained. The gas, apparently, was not analyzed.

(325) Köhler, ibid., 13, 1626 (1880).
(326) Schumann, Ibid., 21, 1079 (1888).

Peterno and Peratoner (327) added titanium tetrachloride to a well-cooled solution of diethylzinc and obtained the molecular compound $TiCl_4 \cdot 2(C_2H_5)_2Zn$. This substance was vigorously decomposed by water, and, besides gas and free zinc, a small quantity of oil was produced. Distillation of the oil gave n-octane, boiling between 120° and 130°, and another liquid fraction which boiled between 220° and 270°. This higher boiling material allegedly contained titanium, apparently identified and determined as the oxide obtained by decomposing the liquid with nitric acid. The analysis of the substance gave values for "titanium" differing by 400% from the theoretical for $(C_2H_5)_4Ti$, and the value found for carbon was in error 40%. The authors admitted that their titanium tetrachloride may not have been pure and the oxide obtained in the analysis may have been that of germanium, whose liquid chloride is known to react with diethylzinc to give an organometallic compound. Undoubtedly these authors did not have in hand an organometallic compound of titanium.

Levy's attempts (328) to prepare organotitanium compounds met with no success. Metallic titanium, either alone or with sodium or potassium showed absolutely no reaction with alkyl iodides. Likewise, titanium metal was inert toward diethylzinc, triethylaluminum, and diethylmercury, even at elevated temperatures. A mixture of dry diethylmercury

(327) Peterno and Peratoner, ibid., 22, 467 (1889).
(328) Levy, Ann. Chim. Phys., [VI] 25, 433 (1892).

and titanium tetrachloride in an atmosphere of carbon dioxide remained unchanged at room temperature. When, however, such a mixture was sealed in a tube and heated to 110° a reaction took place with the formation of ethylmercuric chloride, titanium trichloride, and an unidentified gas which contained neither titanium nor chlorine. The reaction was represented by the equation

$$2TiCl_4 + 2(C_2H_5)_2Hg \longrightarrow 2C_2H_5HgCl + C_4H_{10} + 2TiCl_3$$

At temperatures of 180° or above, the products from the reaction of diethylmercury and titanium tetrachloride were mercury, mercuric chloride, and titanium. These products do not necessarily imply even a momentary formation of ethyltitanium derivatives for at these temperatures diethylmercury is decomposed giving metallic mercury which can reduce titanium tetrachloride to give free titanium and mercuric chloride (328). In the absence of a solvent, titanium tetrachloride and diphenylmercury did not react even at 100°, but in the presence of benzene a reaction took place, and phenylmercuric chloride, biphenyl, and titanium trichloride were formed.

A study by Challenger and co-workers (186) on the reactions of titanium tetrachloride with various organometallic compounds did not lead to the formation of any organotitanium compounds. Phenylmagnesium bromide with titanium tetrachloride in ether solution gave chiefly biphenyl with a little phenol and some p-diphenylbenzene. The black solid product from the reaction contained trivalent titanium. No phenyltitanium

compounds could be isolated. α-Naphthylmagnesium bromide and titanium tetrachloride also formed black precipitates containing lower valent titanium compounds; and the coupling product, bi-α-naphthyl, was obtained. The reaction of chlorobenzene, sodium, and titanium tetrachloride in ether or in boiling benzene produced biphenyl but no organotitanium compounds. Triphenylbismuth with titanium tetrachloride in ether gave a precipitate which, after washing with ether and benzene, was found to be inorganic. The ether-benzene washings yielded diphenylbismuth chloride. Apparently no reduction of the titanium tetrachloride occurred. From a reaction of triphenylantimony with titanium tetrachloride, only triphenylantimony dichloride was obtained. Triphenylarsenic formed a red addition compound with titanium tetrachloride, but upon hydrolysis triphenylarsenic was regenerated.

Browne and Reid (329) mentioned that titanium tetrachloride was reduced by tetraethyllead. When the two were mixed, they reacted readily to give a brown tarry substance tinted purple by titanium trichloride. This reaction took place, also, in benzene.

Some Russian investigators (330) repeated experiments of earlier workers, but no new information was obtained. Titanium tetrachloride and diphenylmercury, when heated

(329) Browne and Reid, J. Am. Chem. Soc., 49, 830 (1927).
(330) Razuvaev and Bogdanov, J. Gen. Chem. (U.S.S.R.), 3, 367 (1933) /C.A., 28, 2340 (1934)/.

together in a sealed tube gave only phenylmercuric chloride, biphenyl, and titanium trichloride. A mixture of phenylmagnesium bromide and titanium trichloride in the absence of a solvent yielded no organotitanium compounds when heated at 180° for three hours. Also, the reaction of a mixture of chlorobenzene, titanium tetrachloride, and sodium failed to produce phenyltitanium compounds.

Pletz (331) claimed to have made organotitanium compounds by the action of n-butyllithium on triethoxytitanium chloride and diethoxytitanium dichloride in benzene solution. The following reactions were given

$$(C_2H_5O)_3TiCl + n\text{-}C_4H_9Li \longrightarrow (C_2H_5O)_3Ti\text{-}n\text{-}C_4H_9 + LiCl$$

$$2(C_2H_5O)_3TiCl + 2n\text{-}C_4H_9Li \longrightarrow (C_2H_5O)_3Ti\text{-}Ti(OC_2H_5)_3 + 2LiCl + n\text{-}C_8H_{18}$$

$$3(C_2H_5O)_2TiCl_2 + 4n\text{-}C_4H_9Li \longrightarrow 4LiCl + 2n\text{-}C_8H_{18} + (C_2H_5O)_2Ti(Cl)Ti(OC_2H_5)_2Ti(Cl)(OC_2H_5)_2$$

The only evidence presented for these reactions was fact that some reduced form of titanium appeared and that when iodine monochloride was added to the mixtures a small quantity of n-butyl iodide was produced. The possibility that the n-butyl iodide may have come from unchanged n-butyllithium, still present in the mixture, was completely ignored. The present study has indicated that n-butyllithium, as well

(331) Pletz, J. Gen. Chem. (U.S.S.R.), 8, 1298 (1938) /C.A., 33, 4195 (1939)/.

as other organolithium compounds and Grignard reagents, form complexes or molecular compounds with the various titanium compounds, and these complexes may remain unchanged for long periods of time but still give characteristic reactions of organolithium compounds, such as the color test with Michler ketone (332).

Attempts were made in this laboratory by J. F. Nelson (333) to prepare organotitanium compounds. Metallic titanium, it was found, underwent no change on long refluxing with a solution of di-p-tolylmercury in xylene. The metal did not react when refluxed with a solution of iodobenzene in tetralin either alone or when small quantities of iodine, di-n-butyl ether, or mercuric chloride were present. Titanium tetrachloride was mixed with ethylmagnesium bromide in ether solution at 0°. When the mixture was allowed to warm up to room temperature, a large volume of gas was evolved. Subsequent to the removal of the ether, the solid product of the reaction was heated in a high vacuum, but no volatile materials were obtained. With phenylmagnesium bromide in ether, titanium tetrachloride reacted to give a black resinous material. Acetyl chloride was added to the mixture but the only products obtained, subsequent to hydrolysis, were biphenyl and inorganic trivalent titanium compounds. Reactions of titanium tetrachloride with ether solutions of phenyllithium

(332) Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925).
(333) Unpublished studies by J. F. Nelson.

led only to a reduction of the titanium tetrachloride and the formation of biphenyl.

All of the organic compounds which contain zirconium are confined to the types in which zirconium is bound directly to oxygen or to nitrogen. No organic compound containing a carbon-zirconium bond has been prepared and only three unsuccessful attempts to prepare such compounds have been reported.

Hinsberg (334) heated zirconium tetrachloride with diethylzinc in a sealed tube. At 100° no reaction occurred. At 180° the zirconium tetrachloride still remained unchanged, but the diethylzinc was decomposed to give metallic zinc and a gas thought to be butane. The same results were obtained when the diethylzinc was diluted with benzene.

Peters (335) found that metallic zirconium did not react with ethyl iodide when the two were heated together in a sealed tube at 200°. Likewise, no reaction took place between zirconium and diethylmercury when they were heated together at 200° in a sealed tube. Mixtures of zirconium tetrachloride with diethylmercury and with diphenylmercury were heated to 200° but remained unchanged.

Venable and Deitz (336) observed a reaction between zirconium tetrachloride and acetylene upon gentle heating,

(334) Hinsberg, Ann., 239, 253 (1887).
(335) Peters, Ber., 41, 3173 (1908).
(336) Venable and Deitz, J. Elisha Mitchell Sci. Soc., 38, Nos. 1 and 2, 74 (1932).

and at 400°, methane and zirconium tetrachloride reacted in the gaseous phase. In both cases, small yields of water-insoluble, unidentified products were obtained which were probably inorganic.

The chemical literature contains no report on organolanthanum compounds. Brief mention has been made (113) that a lanthanum mirror was removed by free methyl radicals. Possibly a methyllanthanum compound was formed.

EXPERIMENTAL

Diphenylmercury and Titanium.--Five grams (0.0141 mole) of diphenylmercury and 0.5 g. (0.0104 g. atom) of titanium powder were placed in a tube under nitrogen, and the tube was sealed. This tube and contents were heated in an oven at 130° for twelve days, but no change took place. When the tube was opened and the contents were extracted with benzene, 4.90 g. (98%) of the diphenylmercury was recovered unchanged.

Diphenylmercury and Lanthanum.--Three grams (0.0084 mole) of diphenylmercury and 0.73 g. (0.0053 g. atom) of lanthanum metal (337) were sealed in a tube under nitrogen and heated in an oven at 135°. After about 60 days the contents of the tube began to darken. After 100 days the tube was opened under nitrogen. Because of the black color of the liquid product, no color test could be made. Dry carbon dioxide was passed through the tube for ten hours, and then the contents were extracted with dry benzene. The benzene removed all of the organic material and left a residue of gray, brittle, metallic particles. The metallic residue was apparently a lanthanum amalgam. It dissolved in dilute hydrochloric acid with the evolution of gas (probably hydrogen)

(337) The metallic lanthanum was obtained from Eimer and Amend, 205 Third Ave., New York, N. Y.

and left droplets of mercury. The benzene soluble products were free of lanthanum, and no benzoic acid could be found subsequent to the treatment with carbon dioxide. A 15% yield of biphenyl (mixed m. p.) was isolated from the benzene soluble products of the reaction. It must be concluded, therefore, that only a decomposition of the diphenylmercury took place and no organolanthanum compound was formed.

Iodobenzene and Lanthanum.--To a Schlenk tube containing 0.50 g. (0.0036 g. atom) of lanthanum metal in small pieces and 1.0 g. (0.0049 mole) of pure iodobenzene was added 5 cc. of ether; and to another tube containing the same quantities of lanthanum and iodobenzene was added 2 cc. of dry benzene. The tubes were sealed and set aside at room temperature. After four months, no change whatsoever had taken place within the tubes.

Miscellaneous Experiments with Zirconium Tetrachloride.--The zirconium tetrachloride used in the experiments reported in this thesis was obtained from the Titanium Alloy Manufacturing Company and was of good quality as the analysis indicates.

Anal. Calcd. for $ZrCl_4$: Zr, 39.2; Cl, 60.8. Found: Zr, 39.3, 39.6; Cl, 59.8.

A solution of 2.8 g. (0.012 mole) of zirconium tetrachloride in 75 cc. of benzene containing a little ether was added to the bromomagnesium derivative of acetomesitylene

(338) prepared from 0.060 mole of ethylmagnesium bromide and 0.055 mole of acetomesitylene in 75 cc. of ether. The mixture was refluxed four hours, but no reaction appeared to take place. The unchanged, crystalline bromomagnesium compound of acetomesitylene was filtered off and hydrolyzed to yield 75% of the original acetomesitylene.

Zirconium tetrachloride ammoniate (339) was prepared by passing gaseous ammonia over 11.6 g. (0.05 mole) of zirconium tetrachloride. When no more ammonia was absorbed, the crystalline product was powdered and added to 200 cc. of liquid ammonia containing 0.22 mole of ethynylsodium. The ethynylsodium was prepared by passing pure, dry acetylene into a solution of 5.0 g. (0.22 g. atom) of sodium in 300 cc. of liquid ammonia (51). The zirconium tetrachloride ammoniate remained in suspension and no reaction appeared to take place. The solid remaining in the flask after the evaporation of the ammonia was a very fine, soft powder. It was totally insoluble in benzene and ether and only slightly soluble in pyridine. Part of the solid was placed in a Soxhlet apparatus and continuously extracted with dry ether, in an atmosphere of nitrogen, for thirty hours. No trace of the solid passed into the ether. In all probability there was no reaction between the zirconium tetrachloride and the sodium acetylide.

(338) Fuson, Fugate and Fisher, J. Am. Chem. Soc., 61, 2362 (1939).
(339) (a) Mathews, J. Am. Chem. Soc., 20, 815 (1898).
(b) Stähler and Denk, Ber., 38, 3611 (1905).

Both $ZrCl_4 \cdot 8NH_3$ (339a) and NaC≡CH (51) have been reported to be entirely insoluble in ether. Water reacted vigorously with the powder leaving the hydroxide as the only compound of zirconium.

Zirconium tetrachloride in water solution did not form an insoluble double salt with benzenediazonium chloride. One-tenth mole of hydrated zirconium tetrachloride was added to 100 cc. of an ice-cold hydrochloric acid solution of 0.1 mole of benzenediazonium chloride. The strongly acid solution was diluted with methanol but no solid separated.

An aqueous hydrochloric acid solution containing 0.064 mole of zirconium tetrachloride was rapidly stirred while powdered aluminum carbide (340) was gradually added. Heat was produced, and much gas was evolved; but no organozirconium compounds could be detected. A reaction like this with mercuric chloride in place of zirconium tetrachloride gave a 19.3% yield of methylmercuric chloride.

Phenylethynyllithium and Zirconium Tetrachloride.--A solution of phenylethynyllithium was prepared according to the method used by Gilman and Young (52) by adding 6.0 g. (0.059 mole) of phenylacetylene to a solution of phenyllithium prepared from 0.055 mole of bromobenzene and excess lithium in 50 cc. of ether. The filtered phenylethynyllithium solution

(340) The aluminum carbide was obtained from Eimer and Amend and appeared to be of a rather low quality. It contained a large quantity of metallic aluminum.

was rapidly stirred while 60 cc. of a saturated benzene solution of zirconium tetrachloride etherate (containing 0.010 mole of $ZrCl_4$) was added dropwise. The reaction mixture gradually turned brown and finally black. When the mixture was hydrolyzed, zirconium hydroxide was obtained. Upon evaporation of the ether-benzene layer, a dark resinous solid was left which did not contain zirconium.

n-Butyllithium and Titanium Tetrachloride.--A solution of 6.55 g. (0.0345 mole) of titanium tetrachloride (redistilled, b. p. 136°) in 50 cc. of dry petroleum ether (b. p. 28-38°) was added dropwise to a solution of 0.138 mole of n-butyllithium in 100 cc. of petroleum ether cooled to -10°. Instantly, a black resinous precipitate was formed. The clear, supernatant petroleum ether, after addition of all of the titanium tetrachloride, gave a negative color test with Michler ketone. The black solid gave a positive color test, and it was also shown to contain lithium. When allowed to dry in the air, the precipitate burned spontaneously. The solid reacted vigorously with dilute acid to give a clear, dark greenish-blue solution. The color of the solution slowly faded upon contact with the air, and was instantly discharged with permanganate or bromine water. The blue water solution gave a black gelatinous precipitate of titanous hydroxide when ammonia was added. A portion of the black solid was hydrolyzed and then extracted with ether, but no ether soluble titanium compound was obtained.

Another experiment was carried out in which 0.05 mole of n-butyllithium in 50 cc. of petroleum ether was added to 0.025 mole of titanium tetrachloride in 50 cc. of petroleum ether. Again, a black resinous solid was obtained which had the same properties as the substance described in the preceding paragraph.

n-Butyllithium and Titanium Tetraethoxide.--Titanium tetraethoxide was prepared according to the directions of Bischoff and Adkins (341). The yield of titanium tetraethoxide from 0.5 mole of titanium tetrachloride was 56%; and the product was a clear, rather viscous liquid which boiled at 149° (15 mm).

A solution of 6.8 g. (0.030 mole) of titanium tetraethoxide in 40 cc. of petroleum ether (b.p. 28-38°) was cooled to -5° and stirred while 0.085 mole of n-butyllithium in 75 cc. of petroleum ether (b.p. 28-38°) was added. The solution was originally colorless but it quickly became green and then changed through dark blue to black. At one stage the reaction mixture was very viscous, and at the end of the reaction, it consisted of a black, finely divided precipitate suspended in the petroleum ether. The blue-black solid gave a strong positive color test, but the petroleum ether gave a negative color test with Michler ketone. The solvent was distilled off under an atmosphere of nitrogen, 75 cc. of dry

(341) Bischoff and Adkins, J. Am. Chem. Soc., 46, 256 (1924).

diethyl ether was added, and the mixture was refluxed for 12 hours. After standing for 18 days the supernatant brown ether solution gave a positive color test and contained both lithium and titanium. The black solid also gave a strong color test and contained lithium and titanium. Possibly organotitanium compounds were present in the black solid. However, no suitable solvent was found for the material.

n-Butyllithium and Zirconium Tetrachloride.--To 100 cc. of a 1.0 molar solution of n-butyllithium (0.10 mole) in petroleum ether (b.p. 28-38°) was added 4.66 g. (0.020 mole) of zirconium tetrachloride. The powder remained in suspension, and no reaction appeared to take place. After seven days, the petroleum ether solution no longer gave a color test with Michler ketone, but the brown precipitate gave a strong color test. When taken into the air on the point of a spatula, the precipitate ignited spontaneously and burned vigorously. The solid product reacted violently with water leaving a precipitate of zirconium hydroxide. The product was also shown to contain lithium.

Phenyllithium and Titanium Tetrachloride.--A suspension of bright yellow, crystalline titanium tetrachloride etherate, $[TiCl_4 \cdot 2(C_2H_5)_2O]$ (342) was prepared by adding 5.70 g. (0.030 mole) of titanium tetrachloride slowly to 35 cc. of ice-cold

(342) Demetrois and Ladikos, Praktika (Akad. Athenon), 5, 449 (1930) [C.A., 27, 3160 (1933)].

ether. To this suspension was added, during thirty minutes, 100 cc. of ether solution containing 0.10 mole of phenyllithium. The reaction mixture first became red; then it rapidly darkened and was finally deep black in color. Upon the addition of water to the reaction mixture, gas continued to be slowly evolved after the first vigorous reaction. The gas collected during five hours was analyzed and found to contain 0.0040 mole of hydrogen. The ether layer was separated, dried, and evaporated to yield 4.12 g. (53.6%) of biphenyl. The black inorganic residue dissolved in dilute acid to give a blue violet solution which was immediately decolorized by bromine water or permanganate. The violet solution also gave a black gelatinous precipitate when treated with ammonia. These properties are characteristic of trivalent titanium.

Phenylmagnesium Bromide and Titanium Tetraethoxide.--A solution of 6.84 g. (0.030 mole) of titanium tetraethoxide in 50 cc. of ether was cooled to -15°. With good stirring, 0.113 mole of phenylmagnesium bromide in 50 cc. of ether was added dropwise over a period of one hour. The mixture gradually darkened during the addition of the Grignard solution, and a brown, finely divided precipitate separated. When the mixture was allowed to warm up to room temperature, the brown precipitate changed to a black, tar-like substance. The supernatant liquid gave a negative color test, but the black tar gave a strong positive color test. The black, ether insoluble material was washed with fresh ether, after decanting

off the original liquid, and the total ether solution was dried over sodium sulfate subsequent to washing with dilute hydrochloric acid. The solvent was removed and 1.90 g. (22%) of biphenyl (mixed m.p.) was obtained.

The black residue reacted vigorously with water or dilute acids to give an aqueous solution containing titanous ions. It was unchanged after heating for five hours in boiling xylene; the color test was still positive and magnesium, titanium, and halogen were still present.

Phenyllithium and Titanium Tetraethoxide.--A solution of 0.10 mole of phenyllithium in 75 cc. of ether was added dropwise during one-half hour to 5.70 g. (0.025 mole) of titanium tetraethoxide in 25 cc. of ether at 0°. The reaction solution remained clear until about two-thirds of the phenyllithium had been added, and then a bright orange, crystalline precipitate suddenly appeared. When stirring was discontinued, the precipitate settled to the bottom leaving a yellow supernatant ether solution which gave a strong positive color test and contained lithium and tetravalent titanium. The orange solid gave a color test, burned spontaneously in the air, reacted violently with water, and was found to contain lithium, halogen, tetravalent titanium but no reduced titanium. Upon standing any length of time or warming up to room temperature, the solid darkened and became sticky. It could not be purified for analysis. After it had turned black, the solid material still gave a positive color test, but it contained

reduced titanium as was shown by the strongly reducing, blue-violet aqueous solution obtained when it was decomposed with dilute acid.

The orange precipitate obtained in another experiment using 0.03 mole of titanium tetraethoxide and 0.12 mole of phenyllithium in 135 cc. of ether had turned completely black within five hours. The black solid was extracted with ether, in a Soxhlet apparatus, under nitrogen for 20 hours. Only biphenyl, 2.95 g. (32%), was obtained from the ether which also gave a negative color test. The unchanged black solid remaining in the thimble gave a strong positive color test, and contained lithium and trivalent titanium.

Phenylmagnesium Bromide and Zirconium Tetrachloride.--To 50 cc. of ether in a flask provided with a mechanical stirrer, a nitrogen inlet, and a dropping funnel was added 5.0 g. (0.021 mole) of zirconium tetrachloride. An exothermic reaction took place with the formation of an etherate of zirconium tetrachloride (343) which was partially soluble in ether. The flask and contents were then cooled to -10°; and 42 cc. of a 2.0 molar ether solution of phenylmagnesium bromide (0.082 mole) was added dropwise to the stirred suspension. At first the mixture became brown, then deep black in color. After standing for several hours at room temperature, the reaction mixture was decomposed with water.

(343) Rosheim and Hertzmann, Ber., 40, 810 (1907).

Much heat was evolved, the black color immediately disappeared; and a white gelatinous precipitate remained. A little gas was liberated, and this was collected over water. Analysis of the gas by the standard absorption and combustion method showed it to consist chiefly of hydrogen, the total yield of which was 0.0032 mole. In all probability, the hydrogen was formed by the action of water on either a lower valent zirconium compound such as ZrX_2 or finely divided zirconium metal. Based on the reaction, $ZrX_2 + H_2O \longrightarrow ZrOX_2 + H_2$, the yield of hydrogen is 15%. From the ether layer was obtained 2.65 g. (41%) of biphenyl (mixed m.p.).

Another experiment was carried out using 0.05 mole of zirconium tetrachloride in 75 cc. of ether and 0.10 mole of phenylmagnesium bromide in 50 cc. of ether. The dark brown supernatant ether solution of the reaction mixture gave a positive color test with Michler ketone and contained magnesium but no zirconium. The mixture was distilled to dryness on the water bath and heated for 3 hours at 90°; and then the black solid remaining in the flask was treated with water. The permanent gas evolved was shown to be hydrogen (0.0098 mole). Ether was also liberated, and 4.33 g. or a 56% yield of oxide biphenyl (m.p., 65-66°) was obtained.

In a duplicate experiment the black solid from the reaction was shown to contain both zirconium and magnesium as well as halogen, and it gave a strong positive color test with Michler ketone.

Phenyllithium and Zirconium Tetrachloride.--A suspension of the etherate from 4.8 g. (0.02 mole) of zirconium tetrachloride in 25 cc. of ether was stirred at -15° while 0.08 mole of phenyllithium in 80 cc. of ether was added during 15 minutes. There was no darkening of the reaction mixture until after the cold bath was removed, and then the mixture gradually became black. After the reaction mixture stood for 11 hours, water was added. The black color was immediately discharged leaving a white precipitate which was identified as $Zr(OH)_4$ since it was inorganic and would not dissolve in excess ammonium chloride solution. The evolved gas was collected over water, and an analysis showed it to consist, mainly, of hydrogen with traces of carbon dioxide, oxygen, and unsaturated hydrocarbons. The yield of hydrogen was 0.0033 mole, or 16% based on the reaction $ZrX_2 + H_2O \longrightarrow ZrOX_2 + H_2$. From the ether layer was obtained 2.72 g. (46%) of biphenyl.

It was found incidentally in these experiments that the etherate of zirconium tetrachloride is much more soluble in benzene than it is in ether. Whereas, an ether solution saturated with $ZrCl_4$ contained only 0.064 mole per liter, the solid crystalline etherate dissolved in dry benzene to the extent of 0.167 mole per liter.

A suspension of 8.0 g. (0.02 mole) of zirconium tetrachloride etherate, assumed to be $ZrCl_4 \cdot 2(C_2H_5)_2O$, in 50 cc. of benzene was stirred at room temperature while 60 cc. of a

1.33 molar ether solution of phenyllithium (0.08 mole) was added dropwise during 45 minutes. First, the etherate all dissolved to give a clear brown solution which gradually changed color through dark brown to black, as the phenyllithium was added. The final black reaction mixture gave a strong color test with michler ketone. To the mixture was added another 0.08 mole of phenyllithium in 60 cc. of ether, and the whole was refluxed for 24 hours under nitrogen and then allowed to stand for seven days. Upon addition of water, the black color was discharged, and the white precipitate which remained was shown to be zirconium hydroxide.

Phenyllithium and Lanthanum Chloride.--Anhydrous lanthanum chloride was prepared by heating hydrated lanthanum chloride, $LaCl_3 \cdot 7H_2O$, in a current of dry hydrogen chloride. The lanthanum chloride was contained in a combustion tube which was heated with an open flame, slowly at first and then for one hour at the full heat of the burner. The anhydrous lanthanum chloride was then powdered and heated in a current of dry nitrogen until free of HCl.

Anal. Calcd. for $LaCl_3$: La, 56.64; Cl, 43.36. Found: La, 56.99; Cl, 42.94.

A suspension of 9.4 g. (0.038 mole) of lanthanum chloride in 50 cc. of ether was stirred while 90 cc. of 1.42 molar phenyllithium (0.128 mole) was added. Apparently, no reaction took place. After three hours, the ether was removed by dis-

tillation and replaced with 50 cc. of dry benzene. When the mixture containing benzene was refluxed it gradually blackened. After standing overnight, the mixture consisted of a dark solid with a supernatant dark brown liquid. The liquid gave a strong positive color test. Dilution of 10 cc. of the liquid with 20 cc. of petroleum ether caused the formation of no precipitate. The liquid reacted vigorously with water and the dark color disappeared. Analysis of 10 cc. aliquots of liquid gave the following values:

Chlorine	0.0000	equivalent	
Bromine	0.0029	"	
Base	0.0156	"	
Total	0.0185	"	
Lithium	0.0166	"	
Lanthanum	0.0029	"	(0.00476 g. atom)
Total	0.0195	"	
Biphenyl	0.0012	mole	

The dark color of the liquid and the excess of lanthanum over the negative ions, indicated in the analyses, suggest that some reduced form of lanthanum was present. Possibly the dark color was due to metallic lanthanum or a lower valent lanthanum bromide in colloidal suspension.

Methyllithium and Zirconium Tetrachloride.--A dry 250 cc. Claisen flask was provided with a rubber-sealed stirrer fitting in the straight neck of the flask, and a dropping funnel in the

bent neck, and the side-arm was connected through a condenser to a gas collector. In the flask was placed 7.0 g. (0.030 mole) of zirconium tetrachloride and 50 cc. of ether, and the apparatus was swept out with nitrogen. To this suspension, rapidly stirred and cooled to -10°, was added from the dropping funnel 110 cc. of ether solution containing 0.12 mole of methyllithium. The addition of the methyllithium required about thirty minutes during which time the solid in the reaction vessel became lemon yellow in color but did not darken. The cold bath was removed, and upon warming up to about 15° the reaction mixture began to turn black. At the same time a rather vigorous evolution of gas set in (accompanied by no noticeable heat effects). After the gas evolution was complete, which required about one-half hour, the apparatus was swept out with nitrogen and the gases were collected over water. Analysis of the gas mixture was made by the standard absorption and combustion method (344). Methane was found to be the only hydrocarbon gas present. Traces of carbon dioxide, unsaturated hydrocarbons, and oxygen were indicated.

(344) A complete description of the analysis need not be given here. Information on gas analysis may be obtained from any standard test on the subject. In the gas analyses described in this thesis, ether vapor was removed with 63% sulfuric acid according to the method of Evans and Field, J. Am. Chem. Soc., 58, 720 (1936). Unsaturated hydrocarbon gases other than ethylene were tested for in each analysis by passing the gas over 82.5% sulfuric acid; and ethylene was determined by absorption in fuming sulfuric acid; see Hurd and Spence, J. Am. Chem. Soc., 51, 3353 (1929).

The yield of methane was 56% on the basis of the methyllithium used.

The black reaction mixture was allowed to stand at room temperature under nitrogen, but no further change took place. After 16 days, the mixture was hydrolyzed by adding distilled water. A vigorous reaction occurred, and another quantity of gas was evolved which was collected over water and analyzed. This second gas contained hydrogen, 0.0048 mole (16% yield), and methane, 0.030 mole (25% yield). As was the case in the reaction involving phenylmagnesium bromide, the hydrogen probably came from the reaction of finely divided zirconium metal or a lower valent zirconium compound with water. The per cent yield is based on the reaction, $ZrX_2 + H_2O \longrightarrow ZrOX_2 + H_2$. Traces of carbon dioxide, oxygen and unsaturated hydrocarbons were also present. The white precipitate remaining in the reaction flask was filtered off and washed with water and shown to be zirconium hydroxide.

The experiment was repeated using 0.020 mole of zirconium tetrachloride and 0.04 mole of methyllithium. A 50% yield of methane was obtained prior to hydrolysis. When the reaction mixture was hydrolyzed. 0.00054 mole (2.7%) of hydrogen was obtained together with 0.0084 mole (21%) of methane.

Methyllithium and Zirconium Tetraphenoxide.--Zirconium tetraphenoxide was prepared from zirconium tetrachloride and phenol in dry benzene solution according to the directions

of Jantsch (345). The product was recrystallized from benzene four times and dried under vacuum but was still not entirely pure.

Anal. Calcd. for $C_{24}H_{20}O_4Zr$: Zr, 19.65. Found: Zr, 18.47, 18.43.

A suspension of 9.26 g. (0.020 mole) of zirconium tetraphenoxide in 25 cc. of ether was cooled to -15° and stirred while 0.08 mole of methyllithium in 60 cc. of ether was added dropwise. A considerable quantity of gas was evolved during the addition of the methyllithium, but the reaction mixture did not darken. After removal of the cold bath, a great deal more gas was evolved as the mixture gradually turned black. The gas obtained prior to hydrolysis contained 0.0555 mole (69% yield) of methane.

Subsequent to hydrolysis, 0.0164 mole (20.5%) of methane and 0.00065 mole (3.3% yield) of hydrogen were obtained.

Methyllithium and Titanium Tetrachloride.--A suspension of 0.025 mole of titanium tetrachloride etherate (from 4.75 g. of $TiCl_4$) in 25 cc. of ether was cooled to -15° and rapidly stirred while 0.10 mole of methyllithium in 75 cc. of ether was added during 30 minutes. The mixture quickly turned black, but no gas was evolved. After all of the methyllithium had been added, the cold bath was removed, and an evolution of gas set in immediately. As the mixture warmed up to room temperature, the gas evolution became

(345) Jantsch, J. prakt. Chem., 115, 7 (1926).

vigorous and was complete in about fifteen minutes. The gas was collected over water and analyzed by the standard combustion and absorption method (344). Methane was the only hydrocarbon gas present, and the yield was 0.064 mole or 64% based on the methyllithium used. Upon hydrolysis of the black reaction mixture, gas was liberated which contained 0.011 mole (10.5% yield) of methane and 0.0025 mole of hydrogen. The hydrogen was probably formed by the action of water on a lower valent titanium compound or on finely divided titanium metal. Based on the reaction, $2Ti + 6H_2O \longrightarrow 2Ti(OH)_3 + 3H_2$ (see ref. 348c), the yield of hydrogen is 7%. A black residue, apparently titanous hydroxide, remained.

Methyllithium and Titanium Tetraethoxide.--A solution of 0.08 mole of methyllithium in 60 cc. of ether was added dropwise over a period of twenty-five minutes to 4.5 g. (0.02 mole) of titanium tetraethoxide in 35 cc. of ether cooled to -10°. The reaction solution remained clear and was colored red-brown until the cold bath was removed, and then it rapidly darkened. After about 15 minutes at room temperature, a slow evolution of gas set in and continued for four hours. The gas was collected over water and an analysis showed the presence of 0.047 mole (58% yield) of methane. The black reaction mixture was hydrolyzed with water and 0.0305 mole (38% yield) of methane and 0.0053 mole (18%) of hydrogen were obtained. A black precipitate of titanous hydroxide remained in the flask.

Methyllithium and Lanthanum Chloride.--A solution of 0.10 mole of methyllithium in 65 cc. of ether was added to a suspension of 8.2 g. (0.033 mole) of lanthanum chloride in 25 cc. of ether at -5°. No reaction took place. When the mixture was allowed to warm up to room temperature, it gradually became colored yellow, and a slow evolution of gas set in. During the course of two days, the white precipitate of lanthanum chloride gave place to a brownish-yellow precipitate which softened and turned to a thick brown syrup and then solidified again. After the fourth day, no more gas was evolved. The gas, collected over water, was analyzed and found to contain 0.0135 mole of methane as the only constituent. On the basis of the methyllithium, this is a 13.5% yield.

After ten days, no further change had taken place in the reaction mixture. The brown solid was filtered under nitrogen and washed with ether until the last washings gave only a slight test for halogen and a negative color test with Michler ketone. The solid, dried under nitrogen, gave a strong positive color test with Michler ketone, and it also gave a color test II with p-iododimethylaniline (346).

(346) Color test II, see ref. 139, is specific for organolithium compounds. However, p-bromodimethylaniline, which has been the reagent used heretofore, gives a negative test with methyllithium; but p-iododimethylaniline gives a positive and highly sensitive test with methyllithium. The sensitivity and applicability of this color test using p-iododimethylaniline is being further studied by Mr. R. V. Christian.

The positive color test II showed that methyllithium was present. The brown material burned spontaneously in the air and reacted violently with water. Qualitative analysis of a water solution of the material showed the presence of halogen, lanthanum, and lithium.

Another reaction was carried out between 11.5 g. (0.047 mole) of lanthanum chloride and 0.15 mole of methyllithium in 175 cc. of ether. The ether was removed from the reaction mixture by distillation; and the brown solid residue was heated at 150° and 30 mm. pressure for one-half hour, but nothing distilled.

Ethylmagnesium Bromide and Titanium Tetrachloride.--A suspension of titanium tetrachloride etherate, prepared by adding 5.70 g. (0.30 mole) of titanium tetrachloride to 50 cc. of ether, was stirred at -15°, and 0.12 mole of ethylmagnesium bromide in 80 cc. of ether was added dropwise. The reaction mixture immediately turned black, and a little gas was evolved. When the mixture was allowed to warm up to room temperature, the gas evolution became quite rapid and was apparently completed in about 2 hours. Analysis of the gas showed the presence of 0.0626 mole (52% yield) of ethane together with small quantities of carbon dioxide, oxygen, and unsaturated hydrocarbons.

The gas which was evolved when the mixture was hydrolyzed with water consisted of 0.0165 mole (13.8% yield) of ethane, 0.0203 mole (45% yield) of hydrogen, and small quantities of

oxygen, carbon dioxide, and unsaturated hydrocarbons. The yield of hydrogen is based on the reaction, $2Ti + 6H_2O \longrightarrow 2Ti(OH)_3 + 3H_2$.

Ethylmagnesium Bromide and Titanium Tetraethoxide.--When 0.12 mole of ethylmagnesium bromide in 55 cc. of ether was added to a stirred solution of 0.03 mole of titanium tetraethoxide in 50 cc. of ether at -15°, the mixture immediately turned black, and gas was slowly given off. As the mixture warmed up to room temperature, after the cold bath was removed, the evolution of gas became more rapid and was apparently complete within three hours. Besides 0.061 mole (51% yield) of ethane, a trace of carbon dioxide, a trace of oxygen, and 0.0034 mole (2%) of ethylene were present. There was no hydrogen.

Hydrolysis of the black reaction mixture with water caused the evolution of 0.0108 mole (9%) of ethane, 0.0158 mole (35% yield) of hydrogen, 0.0027 mole (2%) of unsaturated hydrocarbons, and traces of oxygen and carbon dioxide.

From a duplicate experiment, the yield of ethane, prior to hydrolysis was 58%; and upon hydrolysis, 13.3% of ethane and 0.0153 mole (34%) of hydrogen were obtained. The yields of hydrogen are based on the reaction, $2Ti + 6H_2O \longrightarrow 2Ti(OH)_3 + 3H_2$.

Ethylmagnesium Bromide and Zirconium Tetrachloride.--To a suspension of 7.0 g. (0.030 mole) of zirconium tetrachloride in 50 cc. of ether was added, dropwise, 85 cc. of

an ether solution containing 0.12 mole of ethylmagnesium bromide. During the addition of the Grignard reagent, the reaction mixture turned brown and then black even at -10°, and a little gas was evolved. When the cold bath was removed and the reaction mixture was allowed to warm up to room temperature, the evolution of gas became more rapid but never very vigorous. After two hours, the apparatus was swept out with nitrogen, and the gases were collected over water. Analysis showed the only saturated hydrocarbon gas present to be ethane, 0.048 mole (40%). The gas mixture also contained 0.0024 mole of unsaturated hydrocarbons and traces of carbon dioxide and oxygen. On the basis of the ethylmagnesium bromide, the yield of unsaturated hydrocarbons is only 2% and is therefore insignificant. After two days, the reaction mixture had evolved more gas containing another 0.011 mole of ethane (by analysis) bringing to 48% the total yield of this gas prior to hydrolysis.

Hydrolysis of the black reaction mixture left a residue of zirconium hydroxide and caused the evolution of gas containing 0.0179 mole (60%) of hydrogen, 0.0025 mole (2%) of unsaturated hydrocarbons, and 0.0224 mole (18.7%) of ethane.

The experiment was repeated, and 0.025 mole of zirconium tetrachloride with 0.08 mole of ethylmagnesium bromide were used. The gas evolved prior to hydrolysis was collected during a period of four hours, and a 36% yield of ethane was obtained. By hydrolyzing the reaction mixture, 0.0112 mole

(45%) of hydrogen and 0.0296 mole (37% yield) of ethane were produced. The yields of hydrogen are based on the reaction, $ZrX_3 + H_2O \longrightarrow ZrOX_2 + H_2$.

n-Butylmagnesium Bromide and Zirconium Tetrachloride.-- A solution of 0.24 mole of n-butylmagnesium bromide in 112 cc. of ether was added dropwise to a rapidly stirred suspension of 14 g. (0.060 mole) of zirconium tetrachloride in 75 cc. of ether cooled to -10°. The reaction mixture became black during the addition of the Grignard reagent. After the cold bath was removed, a very slow evolution of gas took place. The ether of the reaction mixture was distilled off on a water bath, and the apparatus was swept out with nitrogen. All gases were collected over water. Besides 0.0261 mole (10.9% yield) of butane; 0.0094 mole of unsaturated hydrocarbons, 0.0081 mole of carbon dioxide, and 0.0133 mole of oxygen were present in the gas mixture. The gas contained no trace of hydrogen.

The gas evolved when the mixture was hydrolyzed contained 0.059 mole (98% yield) of hydrogen and 0.0144 mole (14%) of butane. The hydrolyzed mixture was extracted with ether, and, after drying, the ether extract was fractionally distilled. A fraction boiling between 29° and 34° was shown to contain unsaturated compounds by its ability to rapidly decolorize alkaline permanganate solution and absorb bromine; but no individual compounds were isolated. A 1 cc. fraction which distilled between 80° and 105° appeared to consist of

saturated hydrocarbons and may have contained n-octane; but the quantity of material was so small that it could not be purified.

Ethylmagnesium Bromide and Lanthanum Chloride.—A suspension of 11.2 g. (0.041 mole) of lanthanum chloride in 10 cc. of ether was stirred while 0.152 mole of ethylmagnesium bromide, in 50 cc. of ether, was added. No reaction appeared to take place. Most of the ether was removed, and the remaining mixture of lanthanum chloride and concentrated Grignard solution was heated at 90° for five hours without any apparent change. Finally all of the ether was removed by heating at 110° under 30 mm. pressure. The temperature was then raised to 270° with a pressure of 20 mm., but during one-half hour, nothing distilled over. The mixture in the flask remained white, and there was no evidence that any reaction took place.

DISCUSSION

Some of the general methods which have been used to prepare organometallic derivatives of many of the metals have failed completely when applied to the preparation of organotitanium, zirconium, and lanthanum compounds.

Titanium metal did not react with diphenylmercury, and this behavior is in agreement with the observations of other investigators (58, 329). When diphenylmercury was heated with metallic lanthanum for a long period of time, apparently the only change which took place was a thermal decomposition of the diphenylmercury to form metallic mercury, biphenyl, and other unidentified, tarry products. The lanthanum then combined with the free mercury to form an amalgam.

Although metallic lanthanum reacted readily with water and evolved hydrogen, the metal was inert toward a solution of iodobenzene in ether or in benzene.

Reactions of zirconium tetrachloride in water solution were not extensively investigated, but those tried did not give the desired results. An aqueous solution of zirconium tetrachloride did not form a double salt with benzenediazonium chloride. No organozirconium compounds were obtained when an aqueous hydrochloric acid solution of zirconium tetrachloride was treated with powdered aluminum carbide. However, the

observation of Hilpert and Ditmar (226) was confirmed; aluminum carbide reacted with an acid solution of mercuric chloride and gave methylmercuric chloride.

The most stable inorganic compounds of zirconium are those with highly negative elements or groups. It was thought, therefore, that the most stable organozirconium compounds would be those containing the most acidic organic groups. Attempts were made to attach ethynyl, phenylethynyl, and acetomesitylene groups to zirconium. When the bromomagnesium derivative of acetomesitylene was mixed with zirconium tetrachloride in the presence of ether, there was no evidence that any reaction took place between the two. Ethynylsodium did not react with the ammoniate of zirconium tetrachloride in liquid ammonia. A better zirconium compound for reactions in liquid ammonia would probably be zirconium tetrabromide, which is said to be freely soluble without the formation of ammoniates (347). A reaction readily took place between phenylethynyllithium and zirconium tetrachloride in ether-benzene solution, but no organozirconium compounds were obtained. The course of the reaction was the same as that of similar reactions between zirconium tetrachloride and other organolithium compounds; the zirconium was reduced to a lower state of valence.

In general, the most useful reactions for preparing all

(347) Young, J. Am. Chem. Soc., 57, 1195 (1935).

types of organometallic compounds are the reactions of salts with RM compounds of other metals.

$$MX + RM' \longrightarrow RM + M'X$$

Organometallic compounds of titanium or zirconium were not obtained, however, from the reactions of halides or alkoxides of these metals with organolithium compounds or Grignard reagents. Lanthanum chloride reacted slowly with organolithium compounds, but organolanthanum derivatives could not be isolated from the reactions mixtures. There was no evidence that any reaction took place between lanthanum chloride and ethylmagnesium bromide.

Reactions between n-butyllithium and zirconium tetrachloride, titanium tetrachloride, and titanium tetraethoxide were carried out in petroleum ether solution. With the titanium compounds, black, resinous, solid products were formed. The solid products contained n-butyllithium as evidenced by their positive color tests with Michler ketone. In comparison with RM compounds of other group IV metals it is unlikely that organotitanium compounds, if present, would give positive color tests with Michler ketone. As discussed later, the black color of the precipitates is characteristic of di- and trivalent titanium compounds. The presence of trivalent titanium in the reaction products was confirmed when the mixtures were hydrolyzed with dilute acid. Aqueous solutions with the characteristic blue-violet color of trivalent titanium ions were obtained; and when treated with ammonia

the solutions precipitated black titanous hydroxide. The black precipitates obtained in these reactions prior to hydrolysis, therefore, probably consisted of molecular compounds of the types, $TiX_3 \cdot \underline{n}\text{-}C_4H_9Li$ or $TiX_2 \cdot \underline{n}\text{-}C_4H_9Li$.

The reaction of the insoluble zirconium tetrachloride with n-butyllithium in petroleum ether apparently did not give compounds containing zirconium in a lower state of valence, because the reaction product was not black as are the lower valent zirconium compounds. Probably a molecular compound, $ZrCl_4 \cdot 4\underline{n}\text{-}C_4H_9Li$, was formed, and the reaction proceeded no further. The n-butyllithium was all removed from solution, but the precipitate gave the characteristic reactions of n-butyllithium such as a positive color test with Michler ketone and spontaneous ignition in the air.

Phenyllithium in diethyl ether solution reacted with titanium tetrachloride in much the same way as n-butyllithium reacted with titanium tetrachloride in petroleum ether solution. Black resinous precipitates were formed which contained part of the phenyllithium apparently held in the form of molecular compounds. The reaction between phenyllithium and titanium tetraethoxide gave, first, a bright orange crystalline compound which was stable for a short time at low temperatures. This product was undoubtedly a molecular compound, $Ti(OC_2H_5)_4 \cdot xC_6H_5Li$, since it gave a positive color test with Michler ketone, and it contained both lithium and titanium.

The fact that it was not black was evidence that the titanium was in the tetravalent state. Upon warming up to room temperature, the molecular compound decomposed and gave products analogous with those obtained from the reaction of titanium tetrachloride with phenyllithium. Phenylmagnesium bromide reacted with titanium tetraethoxide and immediately gave a black resinous product. The reactions between titanium tetrachloride or titanium tetraethoxide and RLi or RMgX compounds are best represented by the following series of equations.

$$TiX_4 + RM \longrightarrow TiX_4.xRM \quad \text{.....[I]}$$

$$TiX_4.xRM \longrightarrow TiX_3.(x-1)RM + R. + MX \quad \text{.....[II]}$$

$$TiX_3.(x-1)RM \longrightarrow TiX_3.(x-2)RM + R. + MX \quad \text{.....[III]}$$

$$2R. \longrightarrow R\text{-}R \quad \text{.....[IV]}$$

$$TiX_3.(x-2)RM + H_2O \longrightarrow Ti(OH)_3 + RH + MX + H_2 \quad \text{.....[V]}$$

In accordance with reactions [II], [III], and [IV], biphenyl was formed in yields of from 22 to 54% when phenyllithium or phenylmagnesium bromide was allowed to react with either titanium tetrachloride or titanium tetraethoxide. It is probable that part of the titanium was reduced to the divalent state as indicated in equation [III]. This was evidenced by the black color of the reaction products, which color is typical of divalent titanium compounds (348). Possibly some reduction to metallic titanium also occured.

(348) (a) Georges and Stähler, Ber., 42, 3200 (1909).
(b) Ruff and Neumann, Z. anorg. allgem. Chem., 128, 81 (1923).
(c) Young and Schumb, J. Am. Chem. Soc., 52, 4233 (1930).

Upon hydrolysis, the reaction products evolved hydrogen and gave black precipitates of titanous hydroxide as shown in equation [V]. Divalent titanium compounds react with water to evolve hydrogen and give titanous hydroxide, $Ti(OH)_2$ (348); but $Ti(OH)_2$ liberates hydrogen from water only slowly (348c). If metallic titanium were formed it would be in a state of very fine subdivision and would probably also react with water to liberate hydrogen. The quantities of hydrogen obtained in the reactions involving ethylmagnesium bromide indicated that extensive reduction to metallic titanium occurred. To account for the hydrogen in some cases the reaction, $2Ti + 6H_2O \longrightarrow 2Ti(OH)_3 + 3H_2$, must be assumed. The presence of phenyllithium of phenylmagnesium bromide in the black reaction products was evidenced by positive color tests with Michler ketone. It is possible that organotitanium compounds were formed as unstable intermediate products during the reactions. Equation [IV] could have been written in two steps.

$$TiX_4.xRM \longrightarrow [RTiX_3.(x-1)RM] \longrightarrow TiX_3.(x-1)RM + R.$$

The evidence that the organic groups were expelled as free radicals, R., will be mentioned later.

Zirconium tetrachloride reacted with phenyllithium and with phenylmagnesium bromide in much the same way as did titanium tetrachloride. Black resinous precipitates were formed, and biphenyl was obtained in yields from 40 to 56%. Upon hydrolysis of the reaction mixtures, the black color was immediately discharged; zirconium hydroxide, $Zr(OH)_4$, was

formed; and hydrogen was evolved. These properties are characteristic of the lower valent compounds of zirconium. Zirconium trichloride and zirconium dichloride (349a) and the corresponding bromides (349b) have been described as black solids which react vigorously with water to liberate hydrogen and form zirconium hydroxide. Since the Grignard and organolithium solutions were carefully filtered and were perfectly clear, there was no possibility that the hydrogen obtained upon hydrolysis of the reaction mixtures could have come from metallic lithium or magnesium. Possibly some metallic zirconium was formed and it may have reacted with water and evolved hydrogen. The black reaction products also contained phenylmagnesium bromide or phenyllithium, apparently held in the form of molecular compounds. The RLi and RMgX could not be removed by extraction with ether. The series of equations which follows may account for the products obtained from reactions of zirconium tetrachloride with phenyllithium, phenylmagnesium bromide, or other RLi and RMgX compounds.

$$ZrCl_4 + RM \longrightarrow ZrCl_4.xRM \quad \text{.....[VI]}$$

$$ZrCl_4.xRM \longrightarrow [RZrCl_3.(x-1)RM] + MCl \quad \text{.....[VII]}$$

$$[RZrCl_3.(x-1)RM] \longrightarrow ZrCl_3.(x-1)RM + R. \quad \text{.....[VIII]}$$

$$ZrCl_3.(x-1)RM \longrightarrow [RZrCl_3.(x-2)RM] + MCl \quad \text{.....[IX]}$$

$$[RZrCl_3.(x-2)RM] \longrightarrow ZrCl_3.(x-2)RM + R. \quad \text{.....[X]}$$

$$2R. \longrightarrow R\text{-}R \quad \text{.....[XI]}$$

$$ZrCl_3.(x-2)RM + H_2O \longrightarrow Zr(OH)_4 + RH + MCl + H_2 \quad \text{.....[XII]}$$

(349) (a) Ruff and Wallstein, Z. anorg. allgem. Chem., 128, 96 (1923).
(b) Young, J. Am. Chem. Soc., 53, 2148 (1931).

The organozirconium compounds indicated in equations [VII] and [IX] were possibly formed during the reactions, but they apparently quickly decomposed with the reduction of the zirconium and the expulsion of an organic free radical. Hein (322) has presented evidence that in the spontaneous decomposition of $(C_6H_5)_3CrOH$ in the presence of an alkali metal halide or a hydrohalogen acid, one phenyl group is eliminated as a free phenyl radical.

$$(C_6H_5)_3CrOH + HI \longrightarrow (C_6H_5)_2CrI + C_6H_5\cdot + H_2O$$

This reaction is analogous with reactions [VIII] and [X] above.

The reactions of titanium or zirconium chlorides with methyllithium and with ethylmagnesium bromide were so much like the corresponding reactions with phenyllithium and phenylmagnesium bromide that they need not be discussed in detail. In all cases, black resinous solids were obtained which had properties similar to those already described. There was one important difference between the reactions involving the aliphatic RLi and RMgX compounds and those involving phenyllithium and phenylmagnesium bromide. According to equations [I], [II], and [IV] and equations [VIII], [X], and [XI] biphenyl was formed from phenylmagnesium bromide or phenyllithium. However, in corresponding reactions involving methyllithium, the coupling product, ethane, was not obtained; but the simple hydrocarbon, methane, was obtained in yields of 50 to 60%. In all cases, the hydrocarbon product from the reactions of ethylmagnesium bromide with titanium tetrachloride, titanium tetraethoxide, or zirconium tetrachloride was exclusively ethane. It is probable that these simple hydrocarbon

gases were produced by the action of the corresponding free radicals on the solvent, diethyl ether.

$$R\cdot + (C_2H_5)_2O \longrightarrow RH$$

The studies of Evans and co-workers (106) on the electrolysis of aliphatic Grignard reagents in ether have shown that free methyl and ethyl radicals are able to abstract hydrogen from diethyl ether and form the simple hydrocarbons.

Hydrolysis of the mixtures from the reactions involving methyllithium or ethylmagnesium bromide caused the evolution of hydrogen together with additional quantities of the RH hydrocarbons (equations [V] and [XII]). The RH compounds must have come from the unchanged RLi or RMgX held in the reaction mixtures as complexes. The quantity of hydrogen obtained upon hydrolysis of the reaction mixture from zirconium tetrachloride and n-butylmagnesium bromide is evidence that in this reaction the zirconium was reduced to the divalent state. If it is assumed that the hydrogen came only from the reduction of water by the zirconium compounds, the equation

$$ZrX_2 + H_2O \longrightarrow H_2 + ZrOX_2$$

is necessary to account for the 0.059 mole (0.118 equivalent) of hydrogen which was formed in the reaction involving only 0.06 mole of zirconium tetrachloride. It is also possible that some of the zirconium was reduced to the metal, and this may have reacted with water to produce part of the hydrogen.

The results of the reactions of RLi and RMgX compounds with titanium and zirconium chlorides, titanium ethoxide, and zirconium phenoxide are summarized in Table II.

Table II

Reactions of Titanium and Zirconium Compounds with Methyllithium and Ethylmagnesium Bromide

TiX_4 or ZrX_4	mole	RM	mole	Per cent RH (a)	Per cent RH (b)	Hydrogen (b) mole	Hydrogen (b) %(c)
$TiCl_4$	0.025	CH_3Li	0.10	64.3	10.5	0.0025	7
$Ti(OC_2H_5)_4$	0.02	CH_3Li	0.08	59	38	0.0053	18
$ZrCl_4$	0.03	CH_3Li	0.12	56	25	0.0048	16
$ZrCl_4$	0.02	CH_3Li	0.04	50	21	0.00054	2.7
$Zr(OC_2H_5)_4$	0.02	CH_3Li	0.08	69.4	20.5	0.00065	3.3
$ZrCl_4$	0.025	C_2H_5MgBr	0.08	38	37	0.0112	45
$ZrCl_4$	0.03	C_2H_5MgBr	0.12	48	18.7	0.0179	60
$Ti(OC_2H_5)_4$	0.03	C_2H_5MgBr	0.12	58	13.3	0.0153	34
$Ti(OC_2H_5)_4$	0.03	C_2H_5MgBr	0.12	51	9	0.0158	35
$TiCl_4$	0.03	C_2H_5MgBr	0.12	52	13.8	0.0203	45
$ZrCl_4$	0.06	C_4H_9MgBr	0.24	10.9	14	0.059	98
$TiCl_4$	0.03	C_6H_5Li	0.10	(d)		0.0040	9
$ZrCl_4$	0.02	C_6H_5Li	0.077	(e)		0.0033	17
$ZrCl_4$	0.021	C_6H_5MgBr	0.084	(f)		0.0032	15

(a) Prior to hydrolysis
(b) Produced upon hydrolysis of the reaction mixture.
(c) The per cent yields of hydrogen are arbitrarily based on the reactions, $2Ti + 6H_2O \longrightarrow 2Ti(OH)_3 + 3H_2$ and $ZrX_4 + H_2O \longrightarrow ZrOX_2 + H_2$.
(d) The coupling product, biphenyl, was obtained in a yield of 53.6%.
(e) The yield of biphenyl was 46%.
(f) The yield of biphenyl was 41%.

From this table, it is seen that the total yield of RH hydrocarbon in most cases does not exceed 70 or 80%. It is probable that during the reactions, small quantities of liquid products were formed. In the reaction of n-butylmagnesium bromide with zirconium tetrachloride, the quantity of butane accounts for only 25% of the n-butylmagnesium bromide. Probably, in this case, considerable coupling took place with the formation of octane; although the latter could not be definitely identified.

Methyllithium reacted slowly with lanthanum chloride, and methane was evolved. The yield of methane, however, was only 13.5%; but this quantity of methane is much larger than can be accounted for by hydrolysis of methyllithium by moisture in the apparatus and reagents. Most of the methyllithium apparently formed a complex with the lanthanum chloride, and no further reaction took place. The insoluble product of the reaction was shown to contain methyllithium because it gave a positive color test II which is specific for organolithium compounds, or RM compounds more reactive than the RLi types.

SUMMARY

A collection has been made of all of the known methods for preparing organometallic compounds.

Attempts to prepare organometallic compounds of titanium, zirconium and lanthanum were unsuccessful although several different methods were tried.

The reactions of RLi and RMgX compounds with titanium tetrachloride, titanium tetraethoxide, or zirconium tetrachloride led to a reduction of the titanium or zirconium to lower valence states. The chief hydrocarbon product from the reactions involving phenyllithium or phenylmagnesium bromide was biphenyl. Methane was formed in the reactions of methyllithium with titanium or zirconium chlorides, and ethane was formed in the reactions involving ethylmagnesium bromide.

Lanthanum chloride reacted only slowly with phenyllithium, and some biphenyl was formed. Methyllithium reacted with lanthanum chloride but no organolanthanum compounds could be isolated. A small quantity of methane was produced. No reaction was observed to take place between lanthanum chloride and ethylmagnesium bromide.